



SPECIAL TOPIC: Single-atom Catalysts

Recent research progress in the study of catalytic CO oxidation by gas phase atomic clusters

Li-Na Wang^{1,2,3}, Xiao-Na Li^{1,3} and Sheng-Gui He^{1,2,3*}

ABSTRACT Oxidation of CO into CO₂ is a major solution to reduce CO emission into the atmosphere and to remove CO in fuel gas cleanup. Furthermore, CO oxidation serves as a prototypical reaction for heterogeneous catalysis. This review provides an overview and an update on how to study catalytic CO oxidation at a strictly molecular level by performing well-controlled gas-phase experiments in combination with quantum chemistry calculations. The advances in the unique catalytic reactivity of single-atom cluster catalysts are emphasized. The catalytically active sites and various mechanistic aspects in the redox couples N₂O/CO and O₂/CO for the seemingly simple oxidation reaction are described.

Keywords: CO oxidation, single-atom catalysts, atomic clusters, mass spectrometry, density functional theory calculations

INTRODUCTION

Heterogeneous metal catalysis usually occurs on the surface of a solid material, in which metal components are finely dispersed on a high-surface-area support [1]. The size of metal particles has a great influence on the catalytic performance [2,3]. Smaller metal particles have higher surface free energies, and the metal sites become more active for chemical interactions with the supports and adsorbates [4–9]. An example of such size effect is that gold is chemically inert as bulk material, while dispersed gold particles with nanometer sizes exhibit remarkable catalytic activity [4,10]. A lot of efforts have been devoted to improving the performance of supported metal catalysts by downsizing the metal particles. The ultimate small-size limit for the metal catalysts is the single-atom catalyst (SAC), which contains isolated metal atoms singly dispersed on the supports [2,11]. The SACs

maximize the efficiency of metal atom use and offer great potential for optimizing the activity, selectivity, and stability. Inspired by the successful preparation of Pt₁/FeO_x that exhibits extraordinary catalytic reactivity in CO oxidation [12], many SACs have been designed to promote a variety of heterogeneous reactions, for example, hydrogenation reactions, water-gas-shift reactions, electro-catalytic reactions, and so on. For the rational design of good-performing catalysts, it is important to identify the active sites and understand the mechanisms of catalysis at a molecular level. However, it is extremely challenging to characterize the chemical processes such as the elementary steps involved with dispersedly supported metal atoms in the condensed-phase systems.

Atomic clusters are composed of limited numbers of atoms, and they are experimentally and computationally tractable systems [13–19]. Investigations on cluster reactions in the gas phase can probe the mechanisms of both elementary steps and catalytic cycles under well-controlled and reproducible conditions, thus providing an opportunity to explore the function of SAC or, more generally, to help identify the active parts of single-site catalysts [20–22], the so-called “aristocracies of atoms” [23]. In this review, we survey the catalytic reactivity of gas phase atomic clusters toward CO oxidation to identify the catalytically active parts and uncover the electronic level mechanisms. CO is one of the most common and widely distributed air pollutants. The conversion of CO into CO₂ is of practical importance to reduce CO emission into the atmosphere and to remove CO in fuel gas cleanup. Furthermore, catalytic CO oxidation is a prototypical reaction in heterogeneous systems and represents one type of the well studied reactions in gas-

¹ State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

² University of Chinese Academy of Sciences, Beijing 100049, China

³ Beijing National Laboratory for Molecular Sciences and CAS Research/Education Center of Excellence in Molecular Sciences, Beijing 100190, China

* Corresponding author (email: shengguihe@iccas.ac.cn)

phase catalysis. Many review articles for gas-phase cluster reactivity touched the topic of CO oxidation [15,24–28]. Considering that the research progresses in the studies of CO oxidation by gas-phase clusters have been recently made, we go through the related publications and try to elucidate the mechanistic aspects of the genuine gas-phase catalytic cycles, with an emphasis on cluster-confined single-atom catalysts. The experimentally identified catalytic systems for CO oxidation mediated by bare metal species, metal oxides, metal complexes, or metal-free oxides in the gas phase are listed in Table 1.

CATALYTIC OXIDATION OF CO BY N₂O

N₂O is a potent greenhouse gas and can exacerbate the depletion of stratospheric ozone [63–65]. Conversion of N₂O into N₂ is of particularly practical importance. CO was one of the first gases investigated for eliminating N₂O from automobile exhaust gas (N₂O + CO → N₂ + CO₂). Though the redox reactions are quite exothermic, they do not occur spontaneously at either ambient or raised temperature because of the high activation barriers exceeding 197 kJ mol⁻¹. Therefore, catalysts are necessary to exploit the new pathways with lower barriers. Kappes and

Table 1 Experimentally identified catalytic CO oxidations mediated with gas-phase species

Reaction	Catalyst	Year	Ref.	Reaction	Catalyst	Year	Ref.
CO + N ₂ O → CO ₂ + N ₂	FeO _{0,1} ⁺	1981, 2003, 2005, 2013	[29–32]	2CO + 2NO → N ₂ + 2CO ₂	FeO _{0,1} ⁺	2003	[30]
	PtO _{0,2} ⁺	2001	[33]		OsO _{0,1} ⁺	2003	[30]
	OsO _{0,1} ⁺	2003	[30]	IrO _{0,1} ⁺	2003	[30]	
	IrO _{0,1} ⁺	2003	[30]	FeO _{0,1} ⁺	2003	[30]	
	Pt ₇ O ₀₋₃ ⁺	2004	[30]	CO + NO ₂ → NO + CO ₂	OsO _{0,1} ⁺	2003	[30]
	Pt _n O _m ⁻ (<i>n</i> = 3–6, <i>m</i> = 0–2)	1998	[34]		IrO _{0,1} ⁺	2003	[30]
	GeO _{0,1} ⁺	2005	[31]	Mn ₂ O _{4,5}	2013	[48]	
	SrO _{0,1} ⁺	2005	[31]	Pt _n O _m ⁻ (<i>n</i> = 3–6, <i>m</i> = 0–2)	1998	[34]	
	CaO _{0,1} ⁺	2005	[31]	Au ₆ O _{0,2} ⁻	2002	[49]	
	BaO _{0,1} ⁺	2005	[31]	Au ₂ O _{0,2} ⁻	2001, 2003	[50,51]	
	EuO _{0,1} ⁺	2005	[31]	Ag _n O _{0,4} ⁻ (<i>n</i> = 7, 9, 11)	2004	[52]	
	YbO _{0,1} ⁺	2005	[31]	Au ₃ (CO) ₂₋₅	2011	[53]	
	OsO ₀₋₄ ⁺	2005	[31]	Pd ₆ O ₃₋₅ ⁺	2012	[54]	
	IrO ₀₋₃ ⁺	2005	[31]	AuAl ₃ O ₃₋₅ ⁺	2014	[55]	
	PtO ₀₋₃ ⁺	2005	[31]	2CO + O ₂ → 2CO ₂	PtAl ₃ O ₅₋₇ ⁻	2015	[56]
	Fe(C ₆ H ₆) _{1,2} ³⁺ , FeO(C ₆ H ₆) _{1,2} ⁺	2006	[35]		AuTi ₂ O ₃₋₆	2019	[57]
	Pt ₄ O ₀₋₃ ⁺	2007	[36]	AuVO ₂₋₄	2019	[58]	
	Al ₂ O _{2,3} ⁺	2008	[37]	Cu ₂ VO ₃₋₅ ⁻	2018	[59]	
	Al ₂ O ₂₋₄ ⁻	2008	[37]	CuAl ₄ O ₇₋₉ ⁻	2018	[60]	
	Zr _n O _{2n-1} ⁺ , Zr _n O _{2n} ⁺ (<i>n</i> = 1–4)	2008	[38]	Ni ₂ VO _{4,5} ⁻	2019	[61]	
	Ti ₂ O _{3,4} ⁺	2011	[39]	MnVO ₃₋₅ ⁻	2019	[62]	
	AlVO _{3,4} ⁺	2011, 2018	[40–42]	ZnVO ₃₋₅ ⁻	2019	[62]	
	Rh _n O _m (<i>n</i> = 10–28, <i>m</i> = 0–5)	2012	[43]				
	VO _{2,3}	2013	[44]				
	YAlO _{2,3} ⁺	2013	[45]				
	O _{0,1} NbN ⁺	2019	[46]				
	Si ₂ O _{n-1} ⁺ , Si ₂ O _n ⁺ (<i>n</i> = 3–5)	2017	[47]				

Staley [29] demonstrated the first gas-phase catalytic cycle for the reduction of N_2O with CO, which is mediated by the Fe^+ atomic cation. Subsequently, many catalytic cycles were reported for bare atomic ions [15,22,30–32,66–68], metal clusters [34,36,69–71], and metal oxide clusters [33,37–45,72] in order to characterize the intrinsic factors that influence the reaction outcomes. For example, remarkable charge-effects have been identified when mass-selected cluster ions react with N_2O and CO, such as Pt_4^+ [36,70] and $Zr_nO_{2n}^+/Zr_nO_{2n-1}^-$ ($n = 1-4$) [38,73]. In addition, terminally bonded atomic oxygen radical anions (O_i^-) [74] have been emphasized to account for the high catalytic reactivity toward the N_2O/CO couple [15,24]. Recently, particular role of doping effects has been demonstrated for the reactivity difference of hetero-nuclear cluster systems, such as $ZrScO_4/ZrNbO_5$ [72] and $Y_2O_2^+/YAlO_2^+$ [45]. Furthermore, the ligand effects have also been reported in the $NbN^+/ONbN^+$ system [46].

The $AlVO_3^+/AlVO_4^+$ couple is the first example of hetero-nuclear metal oxide clusters to catalyze CO oxidation by N_2O , which also serves as a classic example to uniquely determine the active site [40]. The $AlVO_4^+$ cluster that was identified to be able to activate the very stable CH_4 molecule [75] can oxidize CO and give rise to CO_2 and $AlVO_3^+$. The formed $AlVO_3^+$ can further react with N_2O to regenerate $AlVO_4^+$, and then the catalytic cycle is closed. These two elementary reactions proceed with high reaction efficiencies of 59% and 65% relative to the collision rates, respectively. Density functional theory (DFT) calculations predicted that during the course of the oxygen atom transfer (OAT), the active site should involve exclusively the terminal $Al-O_i$ unit of $AlVO_4^+$. In contrast, it is both thermodynamically and kinetically unfavorable for the $V=O_i$ moiety of $AlVO_4^+$ to provide an oxygen atom in the oxidation of CO. Recently, gas-phase infrared photo-dissociation spectroscopy unambiguously identified the active site in the $AlVO_n^+/CO/N_2O$ ($n = 3, 4$) redox couples (Fig. 1) [42]. The experimental results

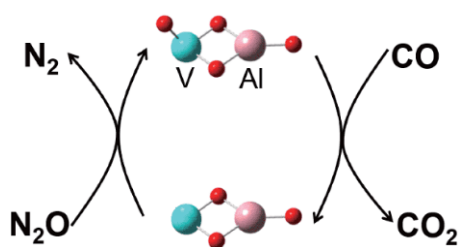


Figure 1 The oxygen atom transfer in the redox couple $AlVO_4^+/CO/N_2O$. Reprinted with permission from Ref. [42]. Copyrights 2018, Wiley-VCH.

confirm the theoretical prediction that the $Al-O_i$, rather than the $V-O_i$ unit catalyzes the reaction.

The efficient OAT reactivity is important to catalyze CO oxidation. Notably, besides the metal-containing clusters mentioned above, the metal-free oxide ions $Si_2O_n^+$ ($n = 2-5$) were recently reported to be capable of mediating three consecutive OAT from N_2O to CO (Fig. 2) [47]. Theoretical investigations showed that the existence of atomic radical anion O^- is crucial for the consecutive OAT processes. The whole redox process is further promoted by the strong electrostatic interaction between the cluster ions and the substrates.

CATALYTIC OXIDATION OF CO BY O_2

Owing to the much stronger bond strength of the O_2 molecule ($O-O = 5.16$ eV) than that of N_2O ($N-O = 1.74$ eV), only a few gas-phase clusters have been demonstrated to catalyze CO oxidation by O_2 [34,49–56,51]. About two years ago, the available gas-phase experiments indicate that a noble metal (NM) atom is indispensable in the catalytic reaction ($2CO + O_2 \rightarrow 2CO_2$) under thermal collision condition, although many NM-free species can catalyze CO oxidation by N_2O . Two or more NM atoms

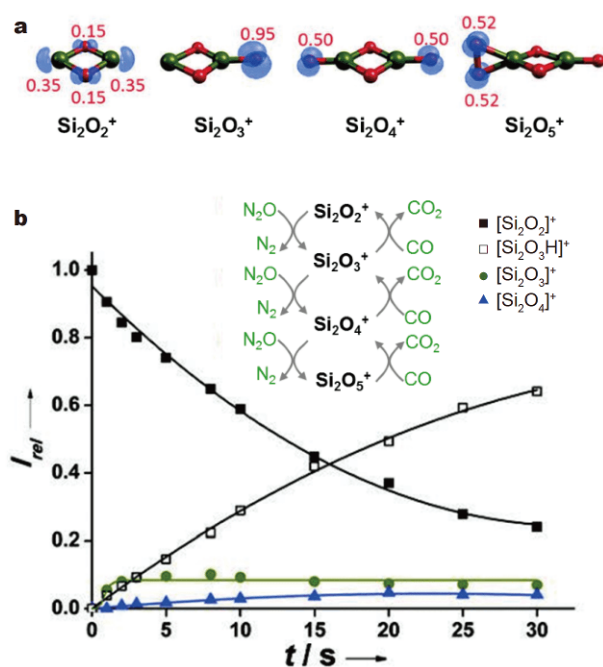


Figure 2 (a) The ground-state structures of $[Si_2O_n]^+$ ($n = 2-5$). The blue isosurfaces indicate the Mulliken spin density distributions, the numerical values of which are denoted in red. (b) Temporal intensity profiles of the reactions between $[Si_2O_n]^+$ and a mixture of N_2O/CO (1:3). Solid lines are generated by fitting the experimental data points. The inset depicts the catalytic redox cycles. Reprinted with permission from Ref. [47]. Copyrights 2017, Wiley-VCH.

are usually needed when CO oxidation by O_2 is mediated by bare or homo-nuclear metal oxide clusters, including Au_2^- [50,51], Au_6^- [49], $Au_3(CO)_{2-5}$ [53], Ag_n^- ($n = 7, 9, 11$) [52], $Pt_nO_m^-$ ($n = 3-6; m = 0-2$) [34], and $Pd_6O_{3-5}^+$ [54]. In 2014, the first example of catalytic CO oxidation by O_2 mediated by gas-phase cluster catalysts with single-noble-metal atoms was identified, which was an important step to understand single-atom catalysis at a strictly molecular level. The single gold atom doped aluminum oxide clusters $AuAl_3O_{3-5}^+$ [55] were mass-selected to react with CO, O_2 , and mixtures of CO and O_2 under thermal collision conditions. The $AuAl_3O_5^+$ cluster can consecutively oxidize two CO molecules to generate $AuAl_3O_4^+$ and then $AuAl_3O_3^+$, and the formed $AuAl_3O_3^+$ can react with one O_2 molecule to regenerate $AuAl_3O_5^+$. The $AuAl_3^{16}O_3^+$ ions interact with a mixture of $C^{16}O$ and $^{18}O_2$ to generate the fully substituted ^{18}O species $AuAl_3^{18}O_{3-5}^+$, which confirms a catalytic cycle for CO oxidation by O_2 . The key to drive the catalysis lies in electron cycling on the gold atom ($Au^+ \leftrightarrow Au^-$) primarily through making and breaking a Au–Al bond. Without the Au atom, pure $Al_3O_4^+$ clusters cannot catalyze CO oxidation and the Ag-atom doped clusters $AgAl_3O_{3-5}^+$ do not work either, which emphasizes that each atom counts. In 2015, single Pt atoms doped hetero-nuclear oxide clusters $PtAl_3O_{5-7}^-$ [56] were also demonstrated to possess the catalytic activity toward CO oxidation by O_2 . Both the single NM atoms and the O^- radical are crucial to drive the catalysis.

The active sites of real-life catalysts could be positive, negative, or neutral in nature. During the past decades, the gas-phase studies of catalytic CO oxidation mainly focused on charged (positive or negative) species, while the neutral catalytic systems were scarcely reported. It has been demonstrated that the cluster charge state can significantly affect the reactivity and reaction mechanisms

[76–78]. Therefore, the investigations on the reactivity of neutral species play a crucial role on understanding the catalytic CO oxidation. However, it is technically challenging to investigate neutral oxide species because it is difficult to ionize and detect neutral oxides without fragmentation in mass spectrometric studies. [79].

In 2012 and 2013, Wang, Yin and Bernstein reported that each of the neutral species VO_3 [44], $VCoO_4$ [80], and $CeAlO_4$ [81] can oxidize one CO molecule and the VO_3/VO_2 couple can catalyze CO oxidation by N_2O [44]. Very recently, benefiting from a homemade time-of-flight mass spectrometer coupled with a vacuum ultraviolet laser system, the catalytic reactivity of neutral Au_1 -doped clusters $AuVO_{2-4}$ [58] and $AuTi_2O_{3-6}$ [57] toward CO oxidation by O_2 has been identified. For Au_1 -V–O system, the $AuVO_{3,4}$ clusters react with CO to generate the adsorption complexes $AuVO_{3,4}CO$ dominantly. Theoretical studies indicate that the oxidation of the trapped CO in $AuVO_{3,4}CO$ to CO_2 is exothermic and the reaction barriers are surmountable to produce $AuVO_{2,3}$ under the condition of elevated temperature. The $AuVO_2$ clusters can react with O_2 to generate $AuVO_4$ and the catalytic cycle for CO oxidation by $AuVO_{2-4}$ is closed. Theoretical results show that the Au oxidation state switches from negative in $AuVO_2$ to positive in product $AuVO_4$, similar to the behavior of Au atom in the cationic $AuAl_3O_{3-5}^+$ systems [55]. In addition, it is identified that the $AuVO_2$ cluster with closed-shell electronic structure can activate molecular O_2 into peroxide O_2^{2-} . For Au_1 -Ti–O system (Fig. 3) [57], the formation of the mobile $AuCO$ moiety modulates the catalytic cycle through promoting CO oxidation and O–O activation. The identification of the neutral Au_1 -cluster catalysts $AuVO_{2-4}$ [58] and $AuTi_2O_{3-6}$ [57] is of importance to reveal the molecular-level reaction mechanisms for related SACs using gold in the condensed-phase studies.

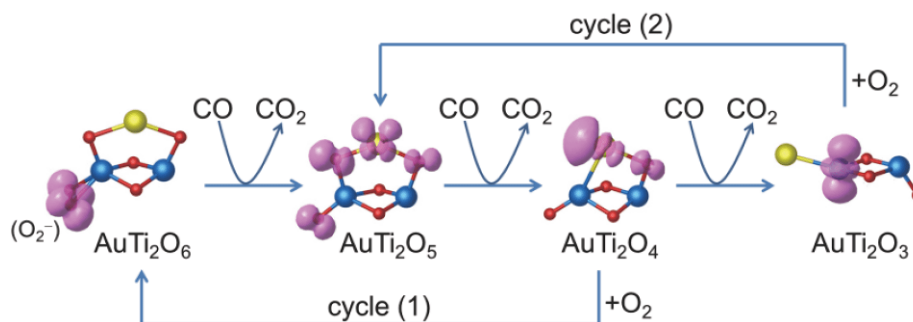


Figure 3 The identified catalytic cycles for CO oxidation mediated with $AuTi_2O_{3-6}$. Reprinted with permission from Ref. [57]. Copyrights 2019, American Chemical Society.

Besides the supported single Au atom catalysts, other NM atoms, such as Pt [82,83], Ir [84,85], Ru [86], Rh [87,88], and Pd [89], are also being actively studied, while the NM-free single atom catalysis of CO oxidation by O₂ has not been experimentally identified in the condensed-phase studies. Recently, the single copper atom doped clusters CuAl₄O₇₋₉⁻ [60] have been demonstrated to catalyze CO oxidation in the gas-phase, which represent the first group of NM free SACs in the field of single atom catalysis. Fig. 4 shows that after the interaction of CuAl₄O₉⁻ with low pressure CO, only CuAl₄O₉CO⁻ can be identified (Fig. 4b). With the increase of CO pressure (Fig. 4c, d), the signal intensity of CuAl₄O₉CO⁻ decreases gradually and CuAl₄O₈⁻ and CuAl₄O₇⁻ are generated, indicating that CuAl₄O₉CO⁻ can react with a second CO

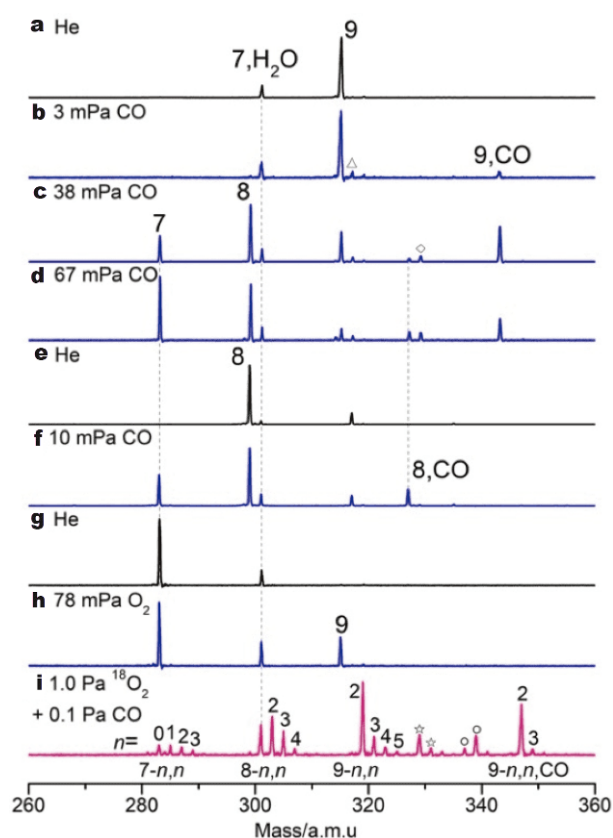


Figure 4 The time-of-flight mass spectra for the reactions of mass-selected CuAl₄O₉⁻ (a), CuAl₄O₈⁻ (e), and CuAl₄O₇⁻ (g) with CO (b–d, and f) or O₂ (h). Panel (i) shows the mass spectrum for the reaction of CuAl₄O₇⁻ with a gas mixture of ¹⁸O₂ and CO. The reaction time is about 2.7 ms. The CuAl₄O_z⁻ and CuAl₄O_zX⁻ (X = CO, H₂O) species are labeled as z and z, X, respectively. Peaks marked with △, ◇, □, and ○ are CuAl₄O₈H₂O⁻, CuAl₄O₇CO(H₂O)⁻, CuAl₄¹⁶O_{8-n}¹⁸O_nCO⁻ (n = 1, 2), and CuAl₄¹⁶O_{8-n}¹⁸O_nO₂⁻ (n = 1, 2), respectively. In Panel (i), CuAl₄¹⁶O_{z-n}¹⁸O_n⁻ is labeled as z–n, n. Reprinted with permission from Ref. [60]. Copyright 2018, Wiley-VCH.

molecule. Fig. 4f shows that CuAl₄O₈⁻ can react with CO to generate CuAl₄O₇⁻, which can react with O₂ to regenerate CuAl₄O₉⁻ (Fig. 4h). The ¹⁶O/¹⁸O exchange in the reaction of CuAl₄¹⁶O₇⁻ with the gas mixture of CO and ¹⁸O₂ (Fig. 5i) confirms that the catalytic oxidation indeed takes place. Such catalysis cannot be mediated with the Al₅O₇₋₉⁻ clusters, highlighting the catalytic importance of Cu atom in CuAl₄O₇₋₉⁻. The identified catalytic cycle is shown in Fig. 5.

The DFT calculations show that the CuAl₄O₉⁻ and CuAl₄O₈⁻ clusters are in the triplet spin states with one O₂⁻ unit (CuAl₄O₉⁻) or O⁻ radical (CuAl₄O₈⁻), while the CuAl₄O₇⁻ has the closed-shell electronic structure, as shown in Fig. 6. The oxygen-rich CuAl₄O₉⁻ cluster is kinetically less favorable to oxidize CO into CO₂ due to the relatively high barrier of O–O bond breaking (I4→TS4→I5→TS5), while the adsorption of another CO on Cu (CuCO) in CuAl₄O₉CO⁻ can stabilize Cu around +I oxidation state to rupture the O–O bond of the superoxide unit (from I6 to I9) and promote CO oxidation into CO₂ [60]. The direct formation of [CuAl₄O₇⁻ + 2CO₂ (P2)] is entropically less favorable (TS15, ΔG₂₉₈ = –2.07 eV) with respect to the generation of [CuAl₄O₈⁻ + CO + CO₂ (P1, ΔG₂₉₈ = –2.21 eV)]. The O⁻ radical in the resulting CuAl₄O₈⁻ can oxidize a CO molecule directly to form CuAl₄O₇⁻ and CO₂. The CuAl₄O₇⁻ cluster with closed-shell electronic structure can activate O₂ to O₂⁻

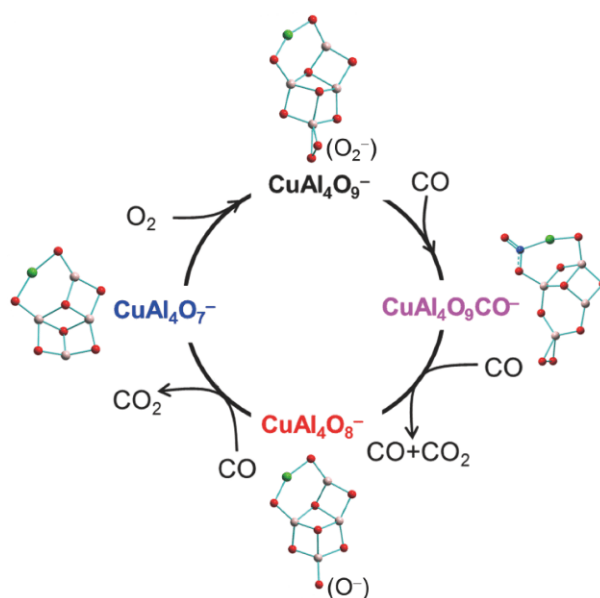


Figure 5 The catalytic cycle of CO oxidation mediated with CuAl₄O₇₋₉⁻ clusters. The structures of CuAl₄O₇₋₉⁻ and a catalytic intermediate CuAl₄O₉CO⁻ are shown. Reprinted with permission from Ref. [60]. Copyright 2018, Wiley-VCH.

unit in $\text{CuAl}_4\text{O}_9^-$. The computations have supported and interpreted the experimental results very well [60].

As NM free hetero-nuclear oxide clusters, the $\text{Cu}_2\text{VO}_{3-5}^-$ [59] and $\text{Ni}_2\text{VO}_{4,5}^-$ [61] can also catalyze CO oxidation by O_2 , as shown in Fig. 7. For the $\text{Cu}_2\text{VO}_{3-5}^-$ system, the Cu_2 dimer functions effectively as a single Au atom in systems such as $\text{AuAl}_3\text{O}_{3-5}^+$ [55] in terms of charge release and storage. The electron cycling on the Cu–Cu unit drives the oxidation catalysis. For the crucial step of molecular O_2 activation, the well charge separation between the negatively charged VO_3^- unit and the positively charged Cu–Cu unit in Cu_2VO_3^- greatly facilitates charge transfer interaction between the Cu–Cu unit and molecular O_2 [59]. Notably, the property of Cu_2VO_3^- with the positively charged Cu–Cu bond is remarkably different from the inert nature of the oxygen deficient system Au_2TiO^- [90] or Au_2VO_2^- [91], which has two separate $\text{Au}^{\delta-}-\text{M}^{\delta+}$ ($\text{M} = \text{Ti}$ or V) bonds.

For the $\text{Ni}_2\text{VO}_{4,5}^-$ system, the Ni_2VO_5^- cluster oxidizes CO to generate an oxygen-deficient product Ni_2VO_4^- . The formed Ni_2VO_4^- can oxidize CO to form a bent CO_2^- unit attached on the Ni_2 -unit in $\text{Ni}_2\text{VO}_3\text{CO}_2^-$, while direct desorption of CO_2 from $\text{Ni}_2\text{VO}_3\text{CO}_2^-$ is thermodynamically hindered, which is different from the kinetically unfavorable oxidation of CO to gas-phase CO_2 by

the $\text{CuAl}_4\text{O}_9^-$ cluster [60]. Note that the $\text{Ni}_2\text{VO}_3\text{CO}_2^-$ species can trap a second CO molecule preferably and then a gas-phase CO_2 molecule can be breezily evaporated to generate $\text{Ni}_2\text{VO}_3\text{CO}^-$. The reaction of the resulting $\text{Ni}_2\text{VO}_3\text{CO}^-$ with O_2 is thermodynamically and kinetically favorable to regenerate Ni_2VO_5^- and a free CO, and then the cycle is closed (Fig. 7b). The CO_2 evaporation from the cluster species typically releases electrons (or negative charges) that are stored originally in the CO_2^- unit. Without the attachment of another CO molecule on $\text{Ni}_2\text{VO}_3\text{CO}_2^-$, the Ni_2 -unit of Ni_2VO_3^- stores the released electrons reluctantly in a single step. However, with CO addition to form $\text{Ni}_2\text{VO}_3\text{CO}_2^-$, the Ni_2 -unit in $\text{Ni}_2\text{VO}_3\text{CO}_2^-$ also acts as the primarily oxidative center but can accept the electrons readily and step by step, behaving like NM atoms. Furthermore, the attached CO can share the burden of the Ni_2 unit to withdraw electrons through the back-donation ($3d \rightarrow 2\pi^*$) interaction [61]. The studies of both $\text{CuAl}_4\text{O}_{7-9}^-$ and Ni_2VO_4^- have demonstrated the CO self-promoting mechanisms: the adsorbed CO can modulate the reaction kinetics (for $\text{CuAl}_4\text{O}_8^- + \text{CO}$) or thermodynamics (for $\text{Ni}_2\text{VO}_4^- + \text{CO}$) to enhance the catalytic performance.

A subtle difference in composition of catalysts will result in great changes in the reactivity, selectivity, or sta-

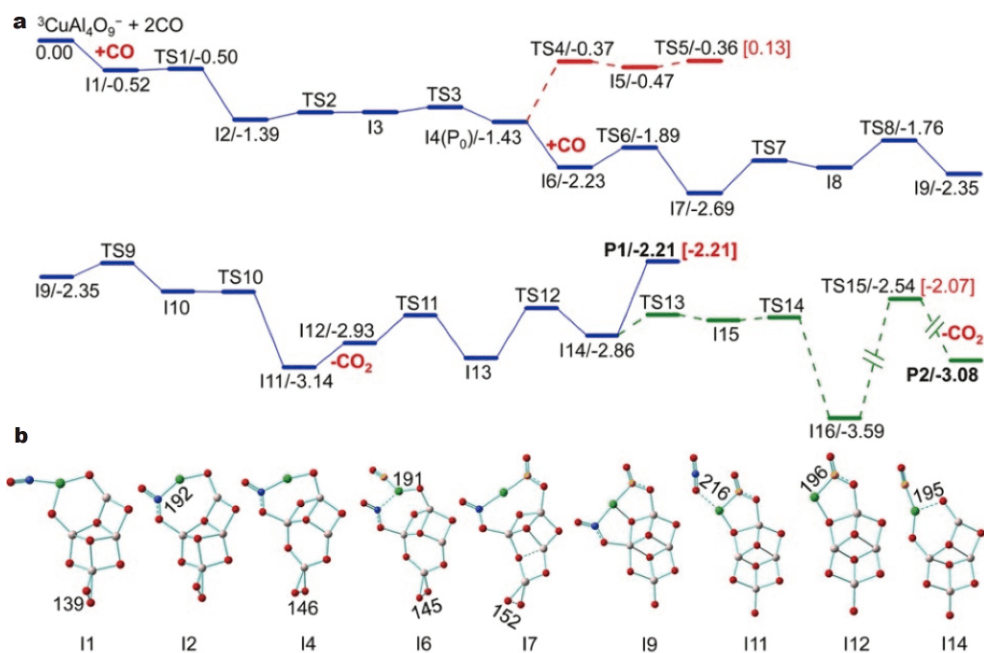


Figure 6 The DFT calculated potential-energy profile for the reaction $\text{CuAl}_4\text{O}_9^- + 2\text{CO}$ on the triplet spin state. The relative energies (ΔH_0 , in eV) for crucial intermediates (Is), transition states (TSs), and products (P1: $\text{CuAl}_4\text{O}_8^- + \text{CO} + \text{CO}_2$; P2: $\text{CuAl}_4\text{O}_7^- + 2\text{CO}_2$) with respect to the separated reactants are given. Bond lengths are given in pm. The red values in brackets are calculated Gibbs free energies at $T = 298$ K [ΔG_{298}]. Reprinted with permission from Ref. [60]. Copyright 2018, Wiley-VCH.

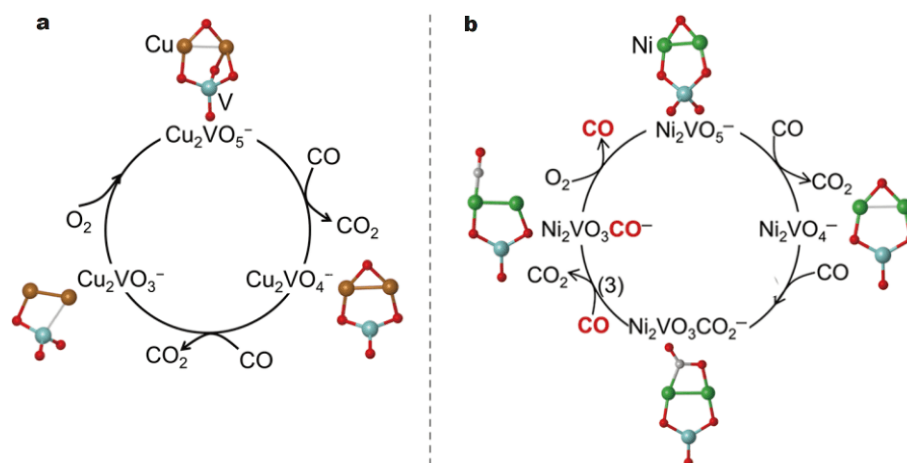


Figure 7 The identified cycles for CO oxidation catalyzed by $\text{Cu}_2\text{VO}_{3.5}^-$ (a) and $\text{Ni}_2\text{VO}_{4.5}^-$ (b). The DFT calculated cluster structures are shown. Reprinted with permission from Refs [59] and [61]. Copyrights 2018, Wiley-VCH and 2019, American Chemical Society.

bility [92–96]. Gas-phase investigations of judiciously doped oxide clusters permit to address the behavior of oxides composed of multiple components. Benefiting from the study of a series of MVO_5^- ($M = \text{V–Zn}$) clusters to catalyze CO oxidation by molecular O_2 , the crucial effects of doping on electronic structure and then the catalytic reactivity of MVO_5^- are successfully rationalized [62]. Experimental results show that among MVO_5^- ($M = \text{V–Zn}$), only the MnVO_5^- and ZnVO_5^- clusters can catalyze CO oxidation by O_2 (Fig. 8). The capability to transfer at least two oxygen atoms consecutively to CO from a single cluster is usually required to catalyze CO oxidation by O_2 . Among the studied MVO_5^- ($M = \text{V–Zn}$) clusters, only the MnVO_5^- and ZnVO_5^- clusters can oxidize CO into gas-phase CO_2 (Reaction 1), while most

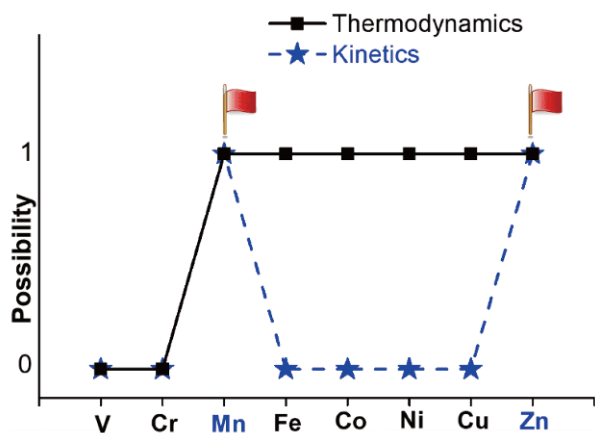
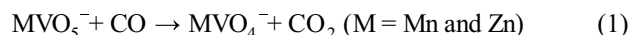


Figure 8 Possibility for the catalytic CO oxidation mediated by MVO_5^- ($M = \text{V–Zn}$) clusters. Reprinted with permission from Ref. [62]. Copyrights 2019, American Chemical Society.

of the MVO_4^- ($M = \text{Mn, Fe, and Ni–Zn}$) clusters can oxidize CO (Reaction 2):



The DFT calculations [62] show that the lowest-lying isomers of the MVO_5^- clusters have similar geometrical structures, while their electronic structures are remarkably different. During CO oxidation, the orbitals of donating (an occupied orbital) and accepting (an unoccupied orbital) electrons are defined as the active orbitals. The reaction enthalpy (ΔH at 0 K) for CO oxidation is highly dependent on the energy gap (ΔE) of the active orbitals, and a relatively larger ΔE value generally corresponds to a thermodynamically less favorable oxidation reaction (Fig. 9). The conclusion also works for CO oxidation by MVO_4^- clusters. The doped clusters MVO_5^- ($M = \text{Cr–Zn}$) have reduced energy gaps of active orbitals than that in host V_2O_5^- , and the OAT process becomes endothermic for MVO_5^- ($M = \text{Mn–Zn}$) ($\Delta H < 0$). The inert nature of the FeVO_5^- , CoVO_5^- , NiVO_5^- , and CuVO_5^- clusters toward CO oxidation is further controlled by reaction kinetics. For the MVO_5^- ($M = \text{V–Fe}$) clusters, the lowest unoccupied molecular orbital (LUMO) that is localized mainly on metal M can overlap with the highest occupied MO (HOMO) of CO, leading to CO adsorption on M through M–CO interaction. The LUMO of MnVO_5^- can overlap well with the HOMO of CO with respect to that of CrVO_5^- and FeVO_5^- , which leads to a kinetically favorable process for CO oxidation by MnVO_5^- . In contrast, the O_f^- radical with unpaired spin density value of about $1.0 \mu_B$ in the NiVO_5^- , CuVO_5^- ,

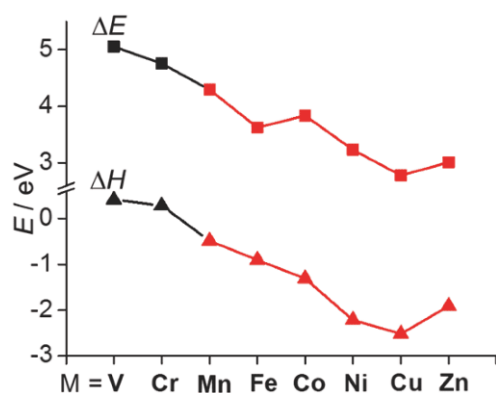


Figure 9 The energy gap (ΔE) of active orbitals for MVO_5^- as well as the DFT calculated enthalpy (ΔH) of reaction $MVO_5^- + CO \rightarrow MVO_4^- + CO_2$. Reprinted with permission from Ref. [62]. Copyrights 2019, American Chemical Society.

and $ZnVO_5^-$ clusters is the preferred site for CO adsorption [62].

The O_t^- radical in $ZnVO_5^-$ can trap and then oxidize CO into CO_2 without a barrier while the oxidation of CO into CO_2 by the O_t^- radical in $NiVO_5^-$ or $CuVO_5^-$ is subject to a small barrier and thus kinetically hindered under thermal collision conditions. Fig. 10 shows that the $NiVO_5^-$ and $CuVO_5^-$ clusters possess two unoccupied orbitals (L+1 and L+2) with the character of O_{2p} orbital ($2p_z$ and $2p_y$ components), while there is only one such orbital (L+1) for $ZnVO_5^-$ (only $2p_z$ component). The single O_{2p} orbital is more facile to overlap with the frontier molecular orbital of CO in the initial interaction between CO and the cluster, which accounts for the higher reactivity of the O_t^- radical in $ZnVO_5^-$. This analysis deepens our perception about the nature of the O^-

radical [74,97] that a highly oxidative O^- species should not only contain a highly localized unpaired electron but also have an unoccupied molecular orbital primarily composed of a single component ($2p_x$, $2p_y$ or $2p_z$) of the O_{2p} atomic orbital.

CONCLUSION AND OUTLOOK

This review summarizes the recent progress in the investigations of catalytic CO oxidation by gas phase atomic clusters, and the unique catalytic performance of the single-atom cluster catalysts is highlighted. The cluster reactivity in CO oxidation can be strongly affected by doping (each atom counts), charge states, metal oxidation states, CO adsorption (CO self-promoted mechanisms), and other issues such as reaction temperature and pressure. The electronic and energetic aspects from quantum chemistry calculations usually support and interpret the experimental findings. In addition, the gas-phase cluster studies during the past two years have discovered the first groups of NM free catalysts for CO oxidation by O_2 under thermal collision conditions. The fundamental mechanisms behind the interesting results are helpful in the design of cost-effective heterogeneous catalysts for both CO oxidation and O_2 reduction. The reported catalytic cycles for CO oxidation by gas phase atomic clusters are far from systematic. Most (>95%) of the experimentally generated atomic clusters are not catalytic toward CO oxidation under thermal collision conditions and it is thus practically difficult to identify new cluster catalysts. To accelerate the experimental identification of new catalytic cycles, more efficient and reliable theoretical predictions and new experimental methods are very helpful. For example, the successful application of machine

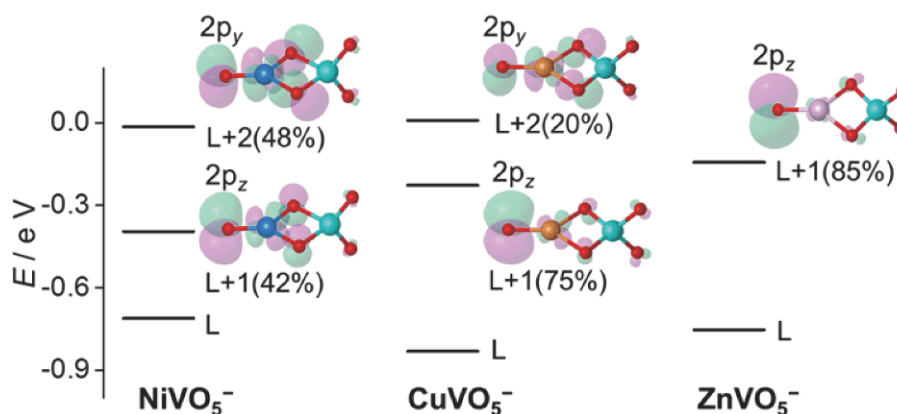


Figure 10 The molecular orbital diagrams for MVO_5^- ($M = Ni, Cu, \text{ and } Zn$). The orbital compositions on O_t atom of the O_t -M bonds are listed in the brackets. $2p_y$ and $2p_z$ denote the $O_t(2p)$ -centered orbital in the direction of y and z axes, respectively. Reprinted with permission from Ref. [62]. Copyrights 2019, American Chemical Society.

learning in cluster science may accelerate the discovery of cluster catalysts. The development of new cluster sources to generate more intense atomic clusters, particularly the hetero-nuclear clusters with more than two metal elements will also be helpful.

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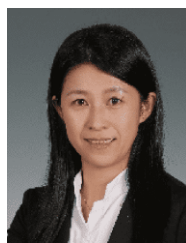
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Author contributions He SG proposed the topic and outline of the manuscript. Wang LN collected the related information and drafted the manuscript. Li XN gave some valuable comments.

Conflict of interest The authors declare no conflict of interest.



Li-Na Wang received her BSc degree in chemistry from Hefei Normal University in 2013, her MSc degree in chemistry from South China University of Technology in 2016, and her PhD degree from the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) in 2019. Her research interests are experimental and theoretical investigations on the reactions of noble-metal-free metal oxide clusters in catalytic CO oxidation.



Xiao-Na Li received her BSc degree in chemistry from Jilin Normal University in 2004, MSc degree in chemistry from Jilin University in 2007, and PhD degree in 2010 from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. She joined the ICCAS in January 2011. Her research interests are experimental and theoretical studies on the reactions of metal oxide clusters in catalytic CO oxidation.



Sheng-Gui He received his BSc degree in physics and PhD degree in chemistry from the University of Science and Technology of China in 1997 and 2002, respectively. After the postdoctoral experience at the University of Kentucky (2002–2005) with Prof. Dennis J. Clouthier and Colorado State University (2005–2007) with Prof. Elliot R. Bernstein, he joined ICCAS in January 2007. His research interests are focused on experimental and theoretical studies on reactive intermediates including free radicals and atomic clusters.

气相原子团簇催化氧化一氧化碳研究新进展

王丽娜^{1,2,3}, 李晓娜^{1,3}, 何圣贵^{1,2,3*}

摘要 将一氧化碳(CO)氧化成二氧化碳(CO₂)是降低大气中CO排放和相关气体净化的有效方法, CO氧化也是非均相催化领域研究的重要模型反应。利用质谱实验结合量子化学理论计算, 研究原子团簇催化氧化CO能够获得相关催化过程的微观反应机制。本文综述了气相原子团簇催化氧化CO的最新研究进展, 重点关注单原子团簇催化剂独特的催化活性。围绕CO + N₂O → CO₂ + N₂和2CO + O₂ → 2CO₂两个催化反应, 本文详细讨论了催化活性位的结构特点以及不同类型的催化反应机制。