

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/275965504>

Thermal Dihydrogen Activation by a Closed-Shell AuCeO₂ + Cluster

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · OCTOBER 2014

Impact Factor: 7.46 · DOI: 10.1021/jz502057n

CITATIONS

6

READS

11

2 AUTHORS:



Jing-Heng Meng

Chinese Academy of Sciences

14 PUBLICATIONS 57 CITATIONS

SEE PROFILE



Sheng-Gui He

Chinese Academy of Sciences

153 PUBLICATIONS 2,503 CITATIONS

SEE PROFILE

Thermal Dihydrogen Activation by a Closed-Shell AuCeO₂⁺ Cluster

Jing-Heng Meng^{†,‡} and Sheng-Gui He^{*,†}

[†]Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

S Supporting Information

ABSTRACT: Laser-ablation-generated AuCeO₂⁺ and CeO₂⁺ oxide clusters were mass-selected using a quadrupole mass filter and reacted with H₂ in an ion trap reactor at ambient conditions. The reactions were characterized by mass spectrometry and density functional theory calculations. The gold–cerium bimetallic oxide cluster AuCeO₂⁺ is more reactive in H₂ activation than the pure cerium oxide cluster CeO₂⁺. The gold atom is the active adsorption site and facilitates the heterolytic cleavage of H₂ in collaboration with the separated O^{2−} ion of the CeO₂ support. To the best of our knowledge, this is the first example of thermal H₂ activation by a closed-shell atomic cluster, which provides molecular-level insights into the single gold atom catalysis over metal oxide supports.

SECTION: Spectroscopy, Photochemistry, and Excited States



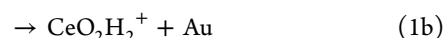
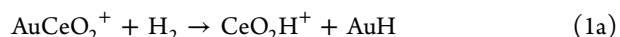
The dihydrogen molecule, with potential applications as a source of clean and renewable energy, is a key reactant in chemical and petrochemical industries. Due to the very strong, apolar covalent bond and low polarizability, H₂ activation is an essential step in nearly all metal catalytic hydrogenation reactions.¹ Much effort has been devoted to understanding H₂ activation at metal centers under mild conditions.^{2–5} Study of gas-phase atomic clusters under well-defined conditions^{6–16} can identify the active sites and uncover the reaction mechanisms that dominate the reactions, which can be crucially important for rational design of efficient catalysts.

Metal oxides have been extensively used as catalytic materials. Many gas-phase studies of thermal H₂ activation by metal oxide species, including MO⁺ (M = Fe, Co, Ni, and Mn),^{17–23} OsO_n⁺ (n = 1–4),²⁴ V₄O₁₀⁺,²⁵ CrO₂⁺,²⁶ VO₂,²⁷ and TaO₄²⁸ have been reported. For the reactions of H₂ with MnO⁺, OsO₄⁺, and V₄O₁₀⁺,^{23–25} the H atom elimination was identified through homolytic cleavage of H₂. In other reactions mentioned above, heterolytic cleavage of H₂ via a four-center transition state was proposed. It should be pointed out that all of these reported metal oxide species that can activate H₂ at ambient conditions have open-shell electronic structures. Herein, we report the first example of H₂ activation by the AuCeO₂⁺ oxide cluster with a closed-shell electronic structure.

Since the breakthrough made by Haruta et al.,^{29,30} gold catalysis has been developing rapidly. Supported gold catalysts have attracted much attention because of their excellent catalytic performance, such as in hydrogenation reactions.^{31,32} Transition-metal oxides including ceria have been widely employed as heterogeneous catalysts or catalyst supports in many processes involving H₂.^{33–37} However, the exact active sites of gold catalysts over metal oxide supports are still controversial. Nakamura, Fujitani, and their co-workers reported that the active sites are located at the perimeter

interface between the gold atoms and the oxide supports.^{3,38} Alternatively, Bus, Lyalin, and their co-workers attributed the active sites to the corner or edge atoms of gold particles.^{39,40} Thus, it is very necessary to study gold-containing heteronuclear oxide clusters in order to understand H₂ activation over metal oxide supported gold catalysts at a molecular level. In this study, the Au–Ce–O heteronuclear cluster cations AuCeO₂⁺ were prepared and reacted with H₂ at room temperature.

The time-of-flight (TOF) mass spectra for interactions of mass-selected AuCeO₂⁺ and CeO₂⁺ cluster cations with H₂ or D₂ in an ion trap reactor are shown in Figure 1. After the interactions of AuCeO₂⁺ with 8 mPa H₂ for about 2.2 ms, three product peaks assigned as CeO₂H⁺, CeO₂H₂⁺, and AuCeO⁺ were observed (Figure 1b), which suggests the three channels below for the reaction of AuCeO₂⁺ with H₂.



The above three channels were confirmed by using the isotopic labeling experiment with D₂ (Figure 1c). In sharp contrast, the CeO₂⁺ cluster is inert toward H₂ because no product peak was observed upon the interactions of CeO₂⁺ with H₂ (Figure 1e).

Pseudo-first-order kinetics is assumed for the ion–molecule reactions in the ion trap reactor because the number of ions is much smaller than that of reactant molecules (see the Supporting Information).⁴¹ For the reactions of AuCeO₂⁺

Received: September 27, 2014

Accepted: October 22, 2014

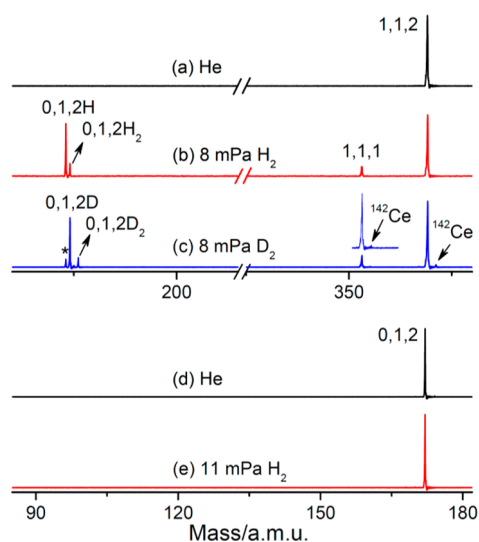


Figure 1. TOF mass spectra for interactions of mass-selected $\text{Au}^{140}\text{CeO}_2^+$ (a–c) and $^{140}\text{CeO}_2^+$ (d,e) with H_2 (b,e) and D_2 (c) in an ion trap reactor for about 2.2 ms. The reactant gas pressures are given, and $\text{Au}_x\text{Ce}_y\text{O}_z^+$ is labeled as x,y,z . The signal labeled with an asterisk in panel c represents the contribution of hydrogen impurity in D_2 gas. The slight instability of the radio frequency potential used to drive the quadrupole mass filter in the experiment caused weak $\text{Au}^{142}\text{CeO}_2^+$ signal in panel c.

with H_2 and D_2 , the total rate constants (k_1), which correspond to relative signal depletion of AuCeO_2^+ cluster ions with respect to the pressure increase of reactant molecules, were estimated and are listed in Table 1. The signal dependence of three product ions on the H_2 or D_2 pressure could be derived and well-fitted with the experimental data (Figure S1, Supporting Information). The branching ratios (BRs) of three channels were determined and are given in Table 1. The total k_1 value of reaction 1 is $(1.6 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is pretty high in comparison with that of thermal H_2 activation by the reported species.^{17–26} The theoretical collision rate constant [$k_{\text{collision}} = 2\pi(e^2\alpha/\mu)^{1/2}$, in which e is the charge of the cluster ion, α is the electric polarizability of the reactant molecule, and μ is the reduced mass]⁴² of reaction 1 is calculated to be $1.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, corresponding to a reaction efficiency (Φ) of $(11 \pm 3)\%$ (Table 1). The kinetic isotope effect (KIE) of reaction 1 is (1.1 ± 0.1) .

Density functional theory (DFT) calculations with the TPSS functional⁴³ were performed to understand the mechanisms of the remarkable reactivity of AuCeO_2^+ toward H_2 . The ground state of AuCeO_2^+ ion (Figure 2, “R”) has a closed-shell electronic structure with the bent Au–O–Ce–O geometric structure. For the lowest-energy structure of the AuCeO^+ cluster (Figure 2, “P3”), the Au atom is bonded with Ce rather than the O atom because the Au–Ce bond energy is larger than that of the Au–O bond (Table S1, Supporting

Information). It is noteworthy that the strong relativistic effect^{44–46} leads to a contracted and stabilized Au 6s orbital, resulting in strong bonding between Au and metal atoms under oxygen-poor conditions. Some isomers for clusters AuCeO_2^+ and AuCeO^+ are given in Figure S2 (Supporting Information). The potential energy profile for reaction 1 at the singlet state is shown in Figure 2. Note that the triplet AuCeO_2^+ is above the singlet state by 1.72 eV (Figure S2, Supporting Information); thus, the reaction mechanism of $\text{AuCeO}_2^+ + \text{H}_2$ at the triplet state is not considered here.

When AuCeO_2^+ reacts with H_2 , the H_2 molecule adsorbs to the positively charged gold atom (+0.70 lel) with a binding energy of 1.13 eV ($\Delta H_{0\text{K}}$). In this process, the H_2 is preactivated, as can be seen from the elongation of the H–H bond from 74 pm in isolated H_2 (R) to 86 pm in intermediate I1. Then, the reaction proceeds in terms of the heterolytic cleavage of the H–H bond (I1 \rightarrow TS1 \rightarrow I2; see the discussion below) by Au^+ species in collaboration with the separated O^{2-} ion. After surmounting TS1 with a small positive free-energy barrier of 0.11 eV ($\Delta G_{298\text{K}}$, Figure S3, Supporting Information), which is the bottleneck of the whole reaction, the subsequent conversions proceed easily with negligible overall barriers. It is noteworthy that the Ce–O bond energy is overestimated (0.44 eV) by the TPSS functional with respect to the experimental data (Table S1, Supporting Information). The energies of I3 and P3 should be lower than those given in Figure 2 because I3 or P3 has one less Ce–O bond than AuCeO_2^+ (R) does. Therefore, all three channels of reaction 1 in the singlet potential energy surface are favorable both thermodynamically and kinetically. The chemistry of the CeO_2^+ ion, which has an open-shell electronic structure and a linear O–Ce–O geometric structure, has been studied by Schwarz and his co-workers.⁴⁷ The DFT calculations indicate that the H_2 activation by CeO_2^+ needs to surmount an overall barrier of about 0.42 eV ($\Delta H_{0\text{K}}$, Figure S4, Supporting Information), which is much larger than the sum of the collisional energy (0.03 eV, see the Supporting Information) and the total vibrational energy of the reactants (0.04 eV, at $T = 298\text{ K}$ by DFT). This is consistent with our experimental result that no product was observed for the reaction of CeO_2^+ with H_2 at room temperature (Figure 1e).

For heterogeneous catalytic reactions, the identification of active sites for binding of reactants is crucially important. For the $\text{AuCeO}_2^+ + \text{H}_2$ system, the cerium atom (+2.01 lel) that is two-fold-coordinated with two O^{2-} ions was also considered as the adsorption site (Figure S5, Supporting Information), while no stable encounter complex could be obtained. Thus, the gold atom (+0.70 lel) that is one-fold-coordinated with the oxygen atom is the effective adsorption site for the H_2 molecule (Figure 2). This is in agreement with our previous studies that the neutral reactants such as CO and CH_4 interact preferentially with noble metal atoms (such as Au, Pt) on non-noble metal oxide clusters.^{48–51}

Table 1. BRs (in %) and Total Rate Constants (k_1 , in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the Reactions of AuCeO_2^+ with H_2 or D_2 Molecules

	BR ^a			k_1	Φ^b	KIE ^c
	$\text{CeO}_2\text{X}^+ + \text{AuX}$	$\text{CeO}_2\text{X}_2^+ + \text{Au}$	$\text{AuCeO}^+ + \text{X}_2\text{O}$			
H_2	63	14	23	1.6	11%	1.1
D_2	63	10	27	1.4	13%	

^aX = H or D. ^bDefined as $k_1/k_{\text{collision}}$, in which $k_{\text{collision}}$ is the theoretical collision rate.⁴² ^cDefined as $[k_1(\text{AuCeO}_2^+ + \text{H}_2)/k_1(\text{AuCeO}_2^+ + \text{D}_2)]$.

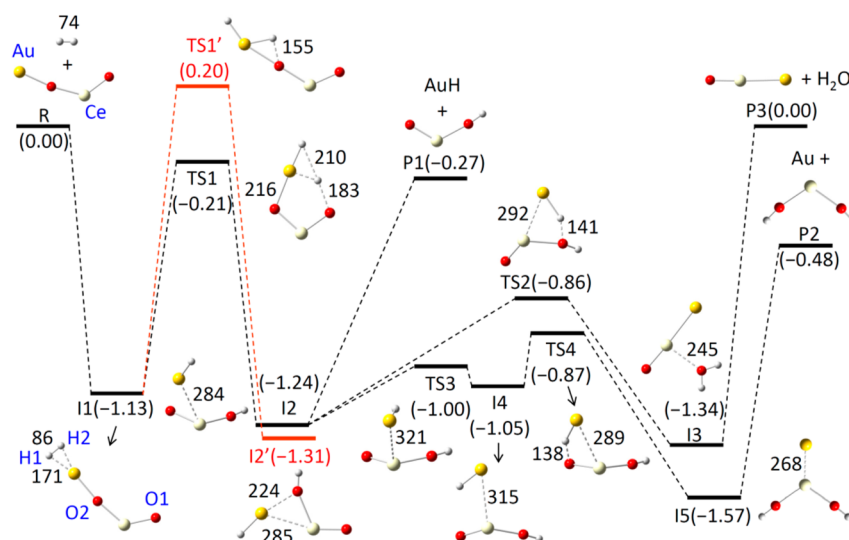


Figure 2. DFT calculated potential energy profile for the reactions $^1\text{AuCeO}_2^+ + ^1\text{H}_2 \rightarrow ^1\text{CeO}_2\text{H}^+ + ^1\text{AuH}$ (P1), $^2\text{CeO}_2\text{H}_2^+ + ^2\text{Au}$ (P2), and $^1\text{AuCeO}^+ + ^1\text{H}_2\text{O}$ (P3). The zero-point vibration corrected energies (ΔH_{0K} in eV) with respect to the separated reactants are given. Some bond lengths in pm are shown.

Natural bond orbital (NBO) charge analysis was carried out for all of the atoms labeled in I1 (Figure 2) along the reaction pathway. The detailed results are given in Tables 2 and S2

Table 2. DFT Calculated NBO Charges (Q , |e|) on the Atoms Labeled in Intermediate I1 along the Reaction Pathway $\text{R} \rightarrow \text{I1} \rightarrow \text{TS1} \rightarrow \text{I2}^a$

	Au	H1	H2	Ce	O1	O2
R	0.70	0.00	0.00	2.01	-1.01	-0.70
I1	0.56	0.08	0.08	2.00	-1.02	-0.70
TS1	0.49	0.02	0.20	1.93	-0.89	-0.74
I2	0.23	-0.03	0.53	1.95	-0.74	-0.93

^aSee details in Figure 2.

(Supporting Information). In I1, each H atom has a +0.08 |e| positive charge, which mostly comes from the Au atom. The empty 6s orbital of the Au atom pulls the electron from the σ orbital of H_2 when forming I1, which weakens the H–H bond. During the decisive step of H_2 activation ($\text{I1} \rightarrow \text{TS1} \rightarrow \text{I2}$), the electron population on the H1 atom (see I1 in Figure 2) increases, and that on the H2 atom decreases significantly (Table 2), which suggests that the H–H bond cleavage occurs in a heterolytic manner.⁵² This process can be attributed to the synergistic effect of the separated Au^+ and O^{2-} (O1) ion pair, resulting in the proton migration to the O^{2-} ion, and the hydride anion forms a chemical bond with the Au^+ ion. The (Au–O2) moiety as the active site to split the H–H bond was also tested, and an overall barrier of 0.2 eV is required (ΔH_{0K} , $\text{I1} \rightarrow \text{TS1}' \rightarrow \text{I2}'$, Figure 2), which is unlikely to happen under our experimental conditions. Note that the gold atom plays another role as the electron container throughout reaction channel 1c, and its charge state can even change from positive to negative (Table S2, Supporting Information), which was also reported in our previous studies of CO oxidation by gold-containing titanium and iron oxide clusters.^{48,49}

Two mechanisms for thermal H_2 activation by metal oxide species with open-shell electronic structures have been reported. The atomic oxygen radical anions, $\text{O}^{\bullet-}$, were proposed as the active species to activate H_2 in a homolytic

manner in the reactions of OsO_4^+ and $\text{V}_4\text{O}_{10}^+$ clusters with H_2 .^{24,25} For other systems, such as TaO_4 with H_2 ,²⁸ the M–O unit was viewed as the active site to induce heterolytic cleavage of the H–H bond. In this study, a new mechanism for H_2 activation by gas-phase metal oxide clusters has been identified; facilitated by the synergistic effect of two separated ions, Au^+ and O^{2-} , the AuCeO_2^+ with a closed-shell electronic structure can heterolytically activate H_2 at ambient conditions. This reaction mechanism parallels the one proposed recently for H_2 activation in condensed-phase studies.^{53–58} The synergistic effect of two separated sites with counter polarity, such as the intra- or intermolecular frustrated Lewis pairs^{53,54} (FLPs) has been utilized to heterolytically activate the H_2 molecule.^{53–57} Here, our gas-phase study indicates that the separated Au^+ and O^{2-} ions in AuCeO_2^+ (Figure 2) can be considered as FLPs to split the H–H bond heterolytically because the cationic gold (Au^+) is a strong Lewis acid⁵⁹ and the O^{2-} ion can be viewed as a Lewis base.

The reactivity improvement by the gold atom in H_2 activation was observed not only for AuCeO_2^+ versus the CeO_2^+ cluster (Figure 1) but also for larger species $\text{AuCe}_2\text{O}_4^+$ versus Ce_2O_4^+ (Figure S6, Supporting Information). The DFT calculations indicate that the $\text{AuCe}_2\text{O}_4^+$ cluster also has a closed-shell electronic structure (Figure S7, Supporting Information) and the H_2 activation by $\text{AuCe}_2\text{O}_4^+$ (Figure S8, Supporting Information) follows a similar mechanism identified for the $\text{AuCeO}_2^+ + \text{H}_2$ reaction system (Figure 2). See the Supporting Information for more discussion on the $\text{AuCe}_2\text{O}_4^+ + \text{H}_2$ reaction. Note that the CeO_2^+ and Ce_2O_4^+ clusters are open-shell species and can efficiently activate $n\text{-C}_4\text{H}_{10}$ and C_2H_6 , respectively,^{47,60} while these two cations are completely inert toward H_2 . The reaction mechanism uncovered in this study (Figure 2) can parallel similar behaviors of H_2 dissociation by gold catalysts over metal oxide supports in the condensed-phase systems.^{3,38,61,62} The analysis of Hückel theory suggested that $\text{O}^{2-}\text{--H}^+\text{--H--Au}$ is a transition-state structure for H_2 dissociation on Au/TiO_2 , and the O^{2-} ion on TiO_2 surface, not directly connecting with Au atom, is more active for H_2 dissociation than the perimeter O^{2-} ion in contact with Au directly.⁶¹ This mechanism is well-supported by the

picture shown in Figure 2 for the gas-phase cluster reaction; gold traps H_2 and splits H_2 in collaboration with the separated O^{2-} ion of the CeO_2 “support” ($\text{I1} \rightarrow \text{TS1} \rightarrow \text{I2}$), while the H_2 splitting by Au^+ and the contacted O^{2-} ion pair ($\text{I1} \rightarrow \text{TS1}' \rightarrow \text{I2}'$) is unfavorable.

In summary, we report the first example of thermal H_2 activation by closed-shell atomic clusters by using mass spectrometry and DFT calculations. The cerium oxide cluster supported single gold atoms can improve the H_2 activation reactivity dramatically in comparison with the unsupported systems. Theoretical calculations indicated that the gold adsorbs H_2 , and then, heterolytic cleavage of H_2 takes place under the synergistic effect of the separated Au^+ and O^{2-} ion pair. This study may shed lights on designing efficient heterogeneous catalysts in H_2 activation.

■ ASSOCIATED CONTENT

● Supporting Information

Detailed description of experimental and theoretical methods and additional experimental and theoretical results, including variations of the relative intensities of the reactant and product cluster ions, DFT calculated isomers, potential energy profiles, and adsorption intermediates, and DFT calculated NBO charges for $\text{AuCeO}_2^+ + \text{H}_2$ reaction; and TOF mass spectra, branching ratios, total rate constants, and relaxed potential energy curves for $\text{AuCe}_2\text{O}_4^+ + \text{H}_2$ reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shengguihe@iccas.ac.cn. Phone: +86-10-62568330. Fax: +86-10-62559373.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the Natural Science Foundation of China (Nos. 21325314 and 21303215), the Major Research Plan of China (Nos. 2013CB834603 and 2011CB932302), and ICCAS (No. CMS-PY-201306).

■ REFERENCES

- (1) Kubas, G. J. Fundamentals of H_2 Binding and Reactivity on Transition Metals Underlying Hydrogenase Function and H_2 Production and Storage. *Chem. Rev.* **2007**, *107*, 4152–4205.
- (2) Fantasia, S.; Egbert, J. D.; Jurčík, V.; Cazin, C. S. J.; Jacobsen, H.; Cavallo, L.; Heinekey, D. M.; Nolan, S. P. Activation of Hydrogen by Palladium(0): Formation of the Mononuclear Dihydride Complex *trans*-[Pd(H_2)(IPr)(PCy₃)]. *Angew. Chem., Int. Ed.* **2009**, *48*, 5182–5186.
- (3) Fujitani, T.; Nakamura, I.; Akita, T.; Okumura, M.; Haruta, M. Hydrogen Dissociation by Gold Clusters. *Angew. Chem., Int. Ed.* **2009**, *48*, 9515–9518.
- (4) Adams, R. D.; Captain, B. Hydrogen Activation by Unsaturated Mixed-Metal Cluster Complexes: New Directions. *Angew. Chem., Int. Ed.* **2008**, *47*, 252–257.
- (5) Spielmann, J.; Buch, F.; Harder, S. Early Main-Group Metal Catalysts for the Hydrogenation of Alkenes with H_2 . *Angew. Chem., Int. Ed.* **2008**, *47*, 9434–9438.
- (6) Böhme, D. K.; Schwarz, H. Gas-Phase Catalysis by Atomic and Cluster Metal Ions: The Ultimate Single-Site Catalysts. *Angew. Chem., Int. Ed.* **2005**, *44*, 2336–2354.
- (7) Schröder, D.; Schwarz, H. Gas-Phase Activation of Methane by Ligated Transition-Metal Cations. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18114–18119.
- (8) Asmis, K. R. Structure Characterization of Metal Oxide Clusters by Vibrational Spectroscopy: Possibilities and Prospects. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9270–9281.
- (9) Lang, S. M.; Bernhardt, T. M. Gas Phase Metal Cluster Model Systems for Heterogeneous Catalysis. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9255–9269.
- (10) Yin, S.; Bernstein, E. R. Gas Phase Chemistry of Neutral Metal Clusters: Distribution, Reactivity and Catalysis. *Int. J. Mass Spectrom.* **2012**, *321–322*, 49–65.
- (11) Zhao, Y.-X.; Wu, X.-N.; Ma, J.-B.; He, S.-G.; Ding, X.-L. Characterization and Reactivity of Oxygen-Centred Radicals over Transition Metal Oxide Clusters. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1925–1938.
- (12) Castleman, A. W., Jr. Cluster Structure and Reactions: Gaining Insights into Catalytic Processes. *Catal. Lett.* **2011**, *141*, 1243–1253.
- (13) Zhai, H.-J.; Wang, L.-S. Probing the Electronic Structure of Early Transition Metal Oxide Clusters: Molecular Models towards Mechanistic Insights into Oxide Surfaces and Catalysis. *Chem. Phys. Lett.* **2010**, *500*, 185–195.
- (14) Gong, Y.; Zhou, M.; Andrews, L. Spectroscopic and Theoretical Studies of Transition Metal Oxides and Dioxygen Complexes. *Chem. Rev.* **2009**, *109*, 6765–6808.
- (15) O'Hair, R. A. J.; Khairallah, G. N. Gas Phase Ion Chemistry of Transition Metal Clusters: Production, Reactivity, and Catalysis. *J. Cluster Sci.* **2004**, *15*, 331–363.
- (16) Roithová, J.; Schröder, D. Selective Activation of Alkanes by Gas-Phase Metal Ions. *Chem. Rev.* **2010**, *110*, 1170–1211.
- (17) Ard, S. G.; Melko, J. J.; Martinez, O.; Ushakov, V. G.; Li, A.; Johnson, R. S.; Shuman, N. S.; Guo, H.; Troe, J.; Viggiano, A. A. Further Insight into the Reaction $\text{FeO}^+ + \text{H}_2 \rightarrow \text{Fe}^+ + \text{H}_2\text{O}$: Temperature Dependent Kinetics, Isotope Effects, and Statistical Modeling. *J. Phys. Chem. A* **2014**, *118*, 6789–6797.
- (18) Baranov, V.; Javahery, G.; Hopkinson, A. C.; Böhme, D. K. Intrinsic Coordination Properties of Iron in FeO^+ : Kinetics at 294 ± 3 K for Gas-Phase Reactions of the Ground States of Fe^+ and FeO^+ with Inorganic Ligands Containing Hydrogen, Nitrogen, and Oxygen. *J. Am. Chem. Soc.* **1995**, *117*, 12801–12809.
- (19) Clemmer, D. E.; Chen, Y.-M.; Khan, F. A.; Armentrout, P. B. State-Specific Reactions of $\text{Fe}^+(\text{a}^6\text{D}, \text{a}^4\text{F})$ with D_2O and Reactions of FeO^+ with D_2 . *J. Phys. Chem.* **1994**, *98*, 6522–6529.
- (20) Schröder, D.; Schwarz, H.; Clemmer, D. E.; Chen, Y.; Armentrout, P. B.; Baranov, V. I.; Böhme, D. K. Activation of Hydrogen and Methane by Thermalized FeO^+ in the Gas Phase as Studied by Multiple Mass Spectrometric Techniques. *Int. J. Mass Spectrom. Ion Processes* **1997**, *161*, 175–191.
- (21) Ryan, M. F.; Fiedler, A.; Schröder, D.; Schwarz, H. Stoichiometric Gas-Phase Oxidation Reactions of CoO^+ with Molecular Hydrogen, Methane, and Small Alkanes. *Organometallics* **1994**, *13*, 4072–4081.
- (22) Schröder, D.; Fiedler, A.; Ryan, M. F.; Schwarz, H. Surprisingly Low Reactivity of Bare FeO^+ in Its Spin-Allowed, Highly Exothermic Reaction with Molecular Hydrogen to Generate Fe^+ and Water. *J. Phys. Chem.* **1994**, *98*, 68–70.
- (23) Ryan, M. F.; Fiedler, A.; Schröder, D.; Schwarz, H. Radical-Like Behavior of Manganese Oxide Cation in Its Gas-Phase Reactions with Dihydrogen and Alkanes. *J. Am. Chem. Soc.* **1995**, *117*, 2033–2040.
- (24) Irikura, K. K.; Beauchamp, J. L. Osmium Tetroxide and Its Fragment Ions in the Gas Phase: Reactivity with Hydrocarbons and Small Molecules. *J. Am. Chem. Soc.* **1989**, *111*, 75–85.
- (25) Yuan, Z.; Zhao, Y.-X.; Li, X.-N.; He, S.-G. Reactions of $\text{V}_4\text{O}_{10}^+$ Cluster Ions with Simple Inorganic and Organic Molecules. *Int. J. Mass Spectrom.* **2013**, *354–355*, 105–112.
- (26) Fiedler, A.; Kretzschmar, I.; Schröder, D.; Schwarz, H. Chromium Dioxide Cation OCrO^+ in the Gas Phase: Structure, Electronic States, and the Reactivity with Hydrogen and Hydrocarbons. *J. Am. Chem. Soc.* **1996**, *118*, 9941–9952.

- (27) Zhou, M.; Wang, C.; Zhuang, J.; Zhao, Y.; Zheng, X. Matrix Isolation Spectroscopic and Theoretical Study of Dihydrogen Activation by Group V Metal Dioxide Molecules. *J. Phys. Chem. A* **2011**, *115*, 39–46.
- (28) Zhou, M.; Wang, C.; Li, Z.; Zhuang, J.; Zhao, Y.; Zheng, X.; Fan, K. Spontaneous Dihydrogen Activation by Neutral TaO₄ Complex at Cryogenic Temperatures. *Angew. Chem., Int. Ed.* **2010**, *49*, 7757–7761.
- (29) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature Far below 0 °C. *Chem. Lett.* **1987**, 405–408.
- (30) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide. *J. Catal.* **1989**, *115*, 301–309.
- (31) McEwan, L.; Juliusa, M.; Roberts, S.; Fletcher, J. C. Q. A Review of the Use of Gold Catalysts in Selective Hydrogenation Reactions. *Gold Bull.* **2010**, *43*, 298–306.
- (32) Mohr, C.; Hofmeister, H.; Radnik, J.; Claus, P. Identification of Active Sites in Gold-Catalyzed Hydrogenation of Acrolein. *J. Am. Chem. Soc.* **2003**, *125*, 1905–1911.
- (33) Carrasco, J.; Vilé, G.; Fernández-Torre, D.; Pérez, R.; Pérez-Ramírez, J.; Ganduglia-Pirovano, M. V. Molecular-Level Understanding of CeO₂ as a Catalyst for Partial Alkyne Hydrogenation. *J. Phys. Chem. C* **2014**, *118*, 5352–5360.
- (34) Rodríguez, J. A.; Senanayake, S. D.; Stacchiola, D.; Liu, P.; Hrbek, J. The Activation of Gold and the Water–Gas Shift Reaction: Insights from Studies with Model Catalysts. *Acc. Chem. Res.* **2013**, *47*, 773–782.
- (35) Vilé, G.; Bridier, B.; Wichert, J.; Pérez-Ramírez, J. Ceria in Hydrogenation Catalysis: High Selectivity in the Conversion of Alkynes to Olefins. *Angew. Chem., Int. Ed.* **2012**, *51*, 8620–8623.
- (36) Zhang, B.; Tang, X.; Li, Y.; Xu, Y.; Shen, W. Hydrogen Production from Steam Reforming of Ethanol and Glycerol over Ceria-Supported Metal Catalysts. *Int. J. Hydrogen Energy* **2007**, *32*, 2367–2373.
- (37) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Active Nonmetallic Au and Pt Species on Ceria-Based Water–Gas Shift Catalysts. *Science* **2003**, *301*, 935–938.
- (38) Nakamura, I.; Mantoku, H.; Furukawa, T.; Fujitani, T. Active Sites for Hydrogen Dissociation over TiO_x/Au(111) Surfaces. *J. Phys. Chem. C* **2011**, *115*, 16074–16080.
- (39) Lyalin, A.; Taketsugu, T. A Computational Investigation of H₂ Adsorption and Dissociation on Au Nanoparticles Supported on TiO₂ Surface. *Faraday Discuss.* **2011**, *152*, 185–201.
- (40) Bus, E.; Miller, J. T.; van Bokhoven, J. A. Hydrogen Chemisorption on Al₂O₃-Supported Gold Catalysts. *J. Phys. Chem. B* **2005**, *109*, 14581–14587.
- (41) Yuan, Z.; Li, Z.-Y.; Zhou, Z.-X.; Liu, Q.-Y.; Zhao, Y.-X.; He, S.-G. Thermal Reactions of (V₂O₅)_nO[−] (*n* = 1–3) Cluster Anions with Ethylene and Propylene: Oxygen Atom Transfer Versus Molecular Association. *J. Phys. Chem. C* **2014**, *118*, 14967–14976.
- (42) Gioumousis, G.; Stevenson, D. P. Reactions of Gaseous Molecule Ions with Gaseous Molecules. V. Theory. *J. Chem. Phys.* **1958**, *29*, 294–299.
- (43) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- (44) Schwarz, H. Relativistic Effects in Gas-Phase Ion Chemistry: An Experimentalist's View. *Angew. Chem., Int. Ed.* **2003**, *42*, 4442–4454.
- (45) Pyykkö, P. Theoretical Chemistry of Gold. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456.
- (46) Jansen, M. The Chemistry of Gold as an Anion. *Chem. Soc. Rev.* **2008**, *37*, 1826–1835.
- (47) Heinemann, C.; Cornehl, H. H.; Schröder, D.; Dolg, M.; Schwarz, H. The CeO₂⁺ Cation: Gas-Phase Reactivity and Electronic Structure. *Inorg. Chem.* **1996**, *35*, 2463–2475.
- (48) Li, X.-N.; Yuan, Z.; He, S.-G. CO Oxidation Promoted by Gold Atoms Supported on Titanium Oxide Cluster Anions. *J. Am. Chem. Soc.* **2014**, *136*, 3617–3623.
- (49) Yuan, Z.; Li, X.-N.; He, S.-G. CO Oxidation Promoted by Gold Atoms Loosely Attached in AuFeO₃[−] Cluster Anions. *J. Phys. Chem. Lett.* **2014**, 1585–1590.
- (50) Zhao, Y.-X.; Li, Z.-Y.; Yuan, Z.; Li, X.-N.; He, S.-G. Thermal Methane Conversion to Formaldehyde Promoted by Single Platinum Atoms in PtAl₂O₄[−] Cluster Anions. *Angew. Chem., Int. Ed.* **2014**, *126*, 9636–9640.
- (51) Li, Z.-Y.; Yuan, Z.; Li, X.-N.; Zhao, Y.-X.; He, S.-G. CO Oxidation Catalyzed by Single Gold Atoms Supported on Aluminum Oxide Clusters. *J. Am. Chem. Soc.* **2014**, *136*, 14307–14313.
- (52) Ochi, N.; Nakao, Y.; Sato, H.; Sakaki, S. Theoretical Study of C–H and N–H σ -Bond Activation Reactions by Ttitanium(IV)-Imido Complex. Good Understanding Based on Orbital Interaction and Theoretical Proposal for N–H σ -Bond Activation of Ammonia. *J. Am. Chem. Soc.* **2007**, *129*, 8615–8624.
- (53) Stephan, D. W. Discovery of Frustrated Lewis Pairs: Intermolecular FLPs for Activation of Small Molecules. *Top. Curr. Chem.* **2013**, *332*, 1–44.
- (54) Wass, D. F.; Chapman, A. M. Frustrated Lewis Pairs Beyond the Main Group: Transition Metal-Containing Systems. *Top. Curr. Chem.* **2013**, *334*, 261–280.
- (55) Flynn, S. R.; Wass, D. F. Transition Metal Frustrated Lewis Pairs. *ACS Catal.* **2013**, *3*, 2574–2581.
- (56) Stephan, D. W.; Erker, G. Frustrated Lewis Pairs: Metal-Free Hydrogen Activation and More. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76.
- (57) Rokob, T. A.; Hamza, A.; Pápai, I. Rationalizing the Reactivity of Frustrated Lewis Pairs: Thermodynamics of H₂ Activation and the Role of Acid–Base Properties. *J. Am. Chem. Soc.* **2009**, *131*, 10701–10710.
- (58) Lu, G.; Zhang, P.; Sun, D.-Q.; Wang, L.; Zhou, K.-B.; Wang, Z.-X.; Guo, G.-C. Gold Catalyzed Hydrogenations of Small Imines and Nitriles: Enhanced Reactivity of Au Surface toward H₂ via Collaboration with a Lewis Base. *Chem. Sci.* **2014**, *5*, 1082–1090.
- (59) Gorin, D. J.; Toste, F. D. Relativistic Effects in Homogeneous Gold Catalysis. *Nature* **2007**, *446*, 395–403.
- (60) Wu, X.-N.; Zhao, Y.-X.; Xue, W.; Wang, Z.-C.; He, S.-G.; Ding, X.-L. Active Sites of Stoichiometric Cerium Oxide Cations (Ce_mO_{2m}⁺) Probed by Reactions with Carbon Monoxide and Small Hydrocarbon Molecules. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3984–3997.
- (61) Sun, K.; Kohyama, M.; Tanaka, S.; Takeda, S. A Study on the Mechanism for H₂ Dissociation on Au/TiO₂ Catalysts. *J. Phys. Chem. C* **2014**, *118*, 1611–1617.
- (62) Yang, B.; Cao, X.-M.; Gong, X.-Q.; Hu, P. A Density Functional Theory Study of Hydrogen Dissociation and Diffusion at the Perimeter Sites of Au/TiO₂. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3741–3745.