# Revealing the Origin of the High Selectivity and Catalytic Activity of Small Ru Clusters in the Methanation of CO

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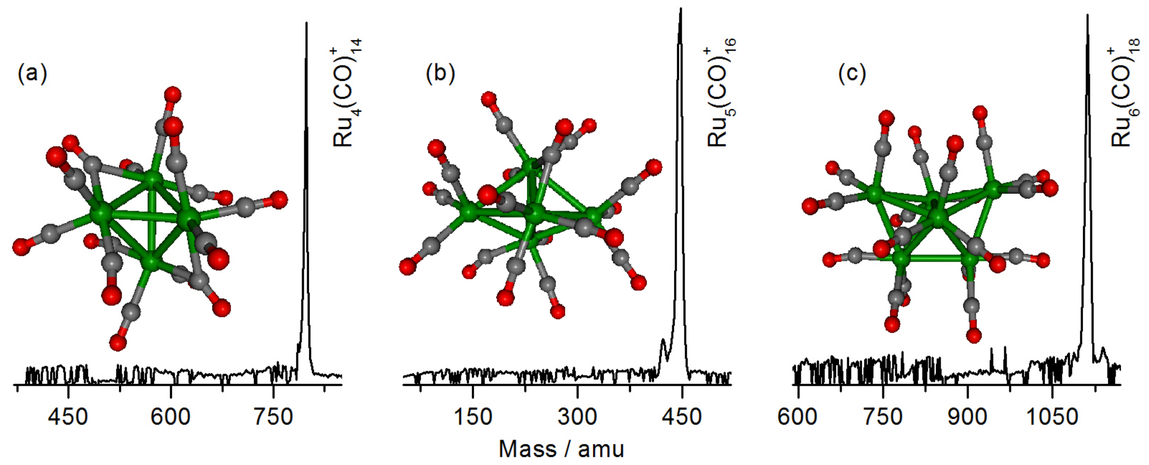
## Introduction

The low temperature polymer electrolyte fuel cell (PEFC) has gained increasing importance for the generation of electrical energy in transportation and decentralized small scale appliances [1]. However, the typically employed hydrogen feed gas usually contains small amounts of CO which can lead to poisoning of the catalyst in the PEFC. One promising approach for CO removal is the catalytic reaction with hydrogen (methanation). At the same time the reaction of $CO_2$ (also present in the feed gas) with $H_2$ should be avoided to prevent excessive hydrogen loss. For such selective CO methanation very small (< 1 nm) supported ruthenium particle catalysts have been shown to be very promising materials [2]. However, the origin of the particular activity and selectivity of sub-nanometer ruthenium particles for fuel cell feed gas purification remains an open question.

Toward this goal we employed gas phase ruthenium clusters $Ru_x^+$ (n = 2 – 6) as model systems and investigated their reactive properties toward molecules contained in typical fuel cell feed gases in an ion trap mass spectrometric experiment and via first-principles density functional theory calculations. Three fundamental properties of these clusters are identified which determine the selectivity and catalytic activity [3,4]: (i) high reactivity toward CO in contrast to inertness in the reaction with $CO_2$; (ii) promotion of cooperatively enhanced $H_2$ coadsorption and dissociation on pre-formed ruthenium carbonyl clusters, i.e. no CO poisoning occurs; and (iii) the presence of low coordinated Ru-atom sites, which are particularly active for $H_2$ coadsorption and activation. Furthermore, comprehensive theoretical investigations provide mechanistic insight into the CO methanation reaction and discover a reaction route involving the formation of a formyl-type intermediate.

## $CO/CO_2$ Selectivity

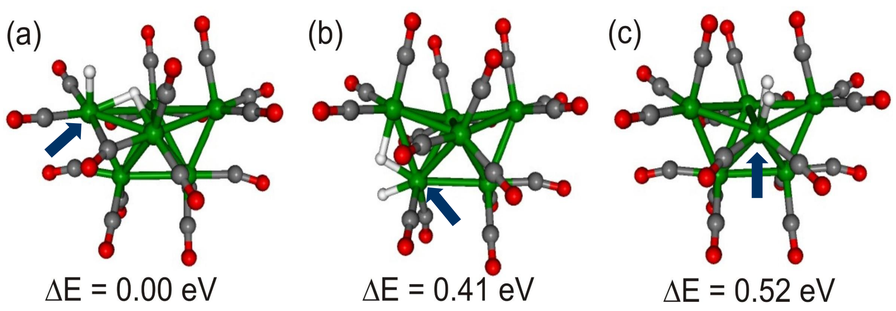



Product mass spectra obtained after reaction of (a) $Ru_4^+$ (b) $Ru_5^+$ and (c) $Ru_6^+$ with CO for a reaction time of 0.1 s. Also displayed are the corresponding DFT structures of the most abundant products. Ru, C, O and H are indicated by green, gray, red, and white spheres, respectively [3, 4].

$Ru_4^+ + CO \rightarrow Ru_4(CO)_{14}^+$
$Ru_5^+ + CO \rightarrow Ru_5(CO)_{16}^+$
$Ru_6^+ + CO \rightarrow Ru_6(CO)_{18}^+$

$Ru_x^+ + CO_2 \rightarrow$ no reaction

## Low Coordinated Ru Atom Sites

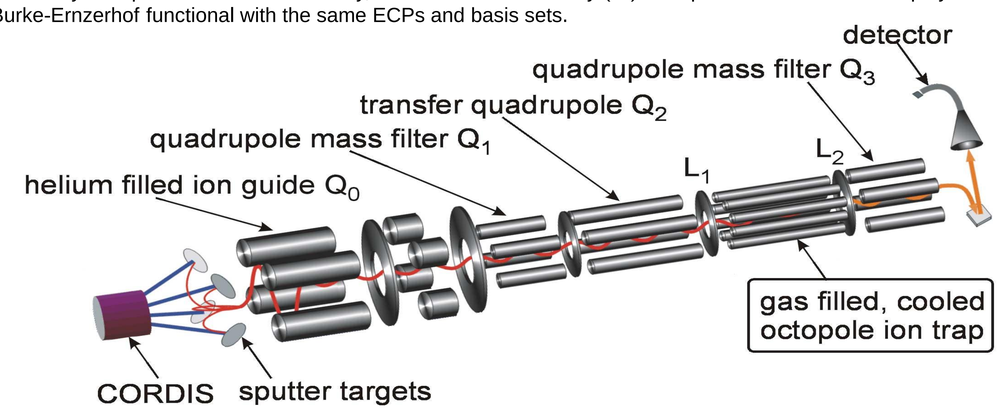



Optimized structures of $Ru_6(CO)_{17}H_2^+$ comprising $H_2$ adsorbed at a (a) three-fold, (b) four-fold, and (c) five-fold coordinated Ru atom, respectively [4].

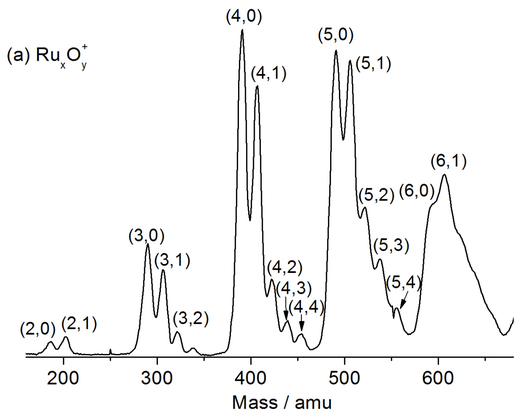
## Experimental and Theoretical Methods

The experimental setup consists of an octopole ion trap inserted into a multiple quadrupole mass spectrometer arrangement. The metal clusters are produced by an ion sputtering source (CORDIS) and are mass-selected in a first quadrupole mass filter before entering the octopole ion trap. The trap is filled with about 1-2 Pa total pressure of helium and the reactive gases. After a chosen reaction time all ions, intermediates, and final products are extracted from the ion trap and are subsequently mass-analyzed by a second quadrupole mass filter $Q_3$.

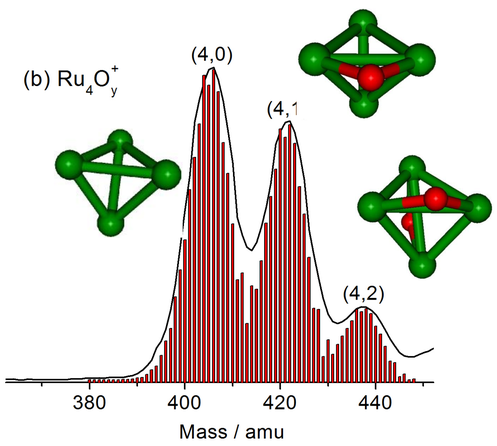
The structural properties of the ruthenium cluster cations and their reactivity were studied using DFT with the hybrid B3LYP functional. For the Ru atoms the Stuttgart group relativistic effective core potentials (ECPs) were employed together with the triple-ζ-valence-plus-polarization basis sets which were also used for the C, O, and H atoms. In order to improve efficiency for the larger carbonyl complexes and their reactivity, the resolution of identity (RI)-DFT procedure has been employed using the Perdew-Burke-Ernzerhof functional with the same ECPs and basis sets.




## Generation of $Ru_x^+$ Clusters

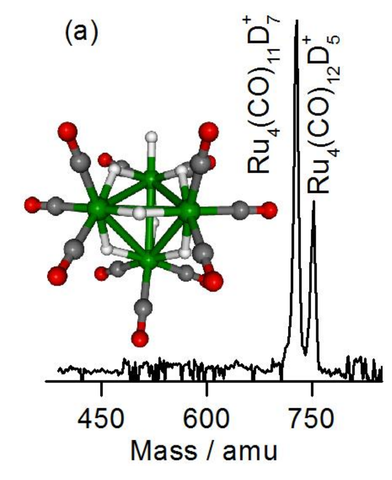


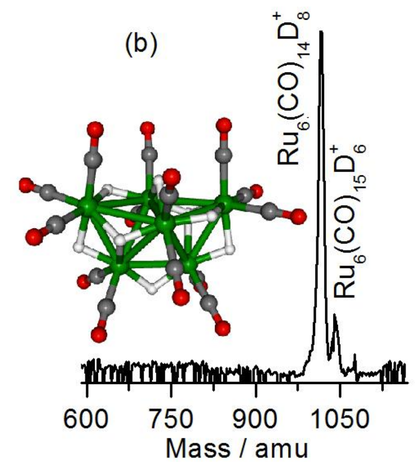

(a) Ruthenium and ruthenium-oxide cluster distribution generated by the CORDIS sputter source. The mass peaks are denoted with (x,y) corresponding to complexes of the stoichiometry $Ru_xO_y^+$.

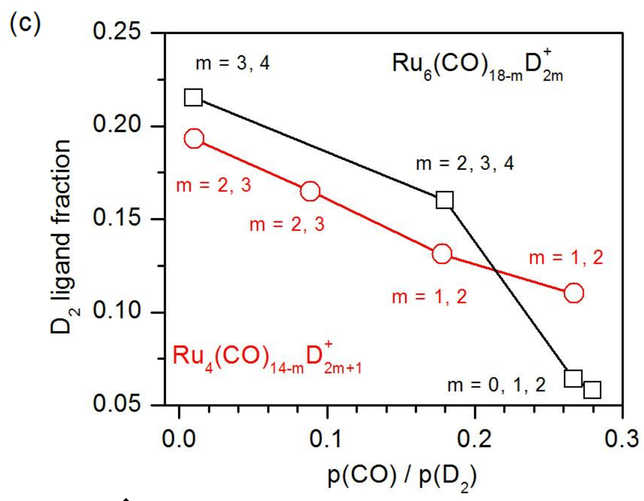



(b) Enlarged view of the cluster signal in the mass range between 380 and 450 amu. The bars represent the calculated mass distribution of $Ru_4O_y^+$ (y = 0 - 2) derived from the natural abundance of the ruthenium isotopes.

## Cooperative Coadsorption of CO and $D_2$



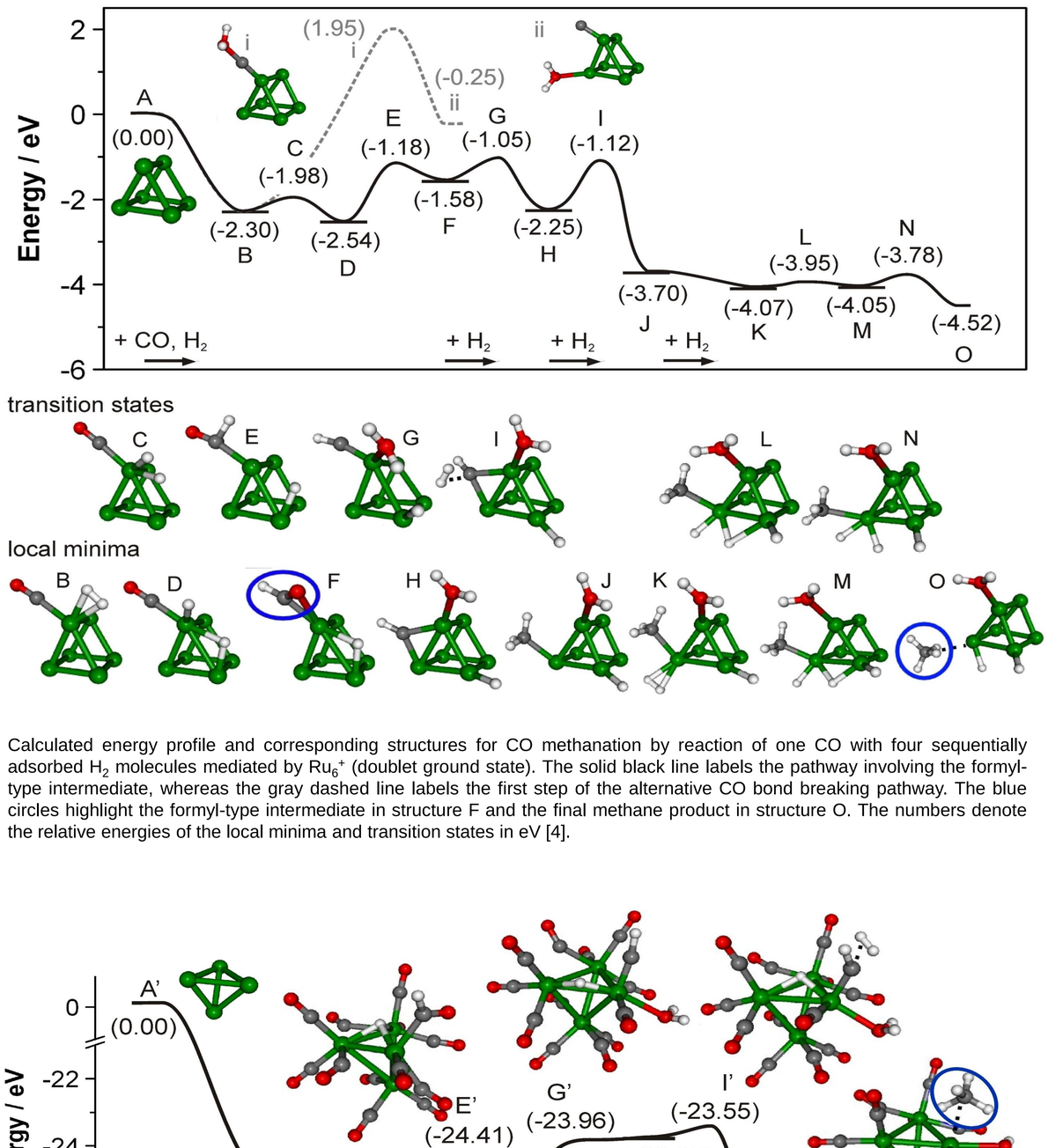



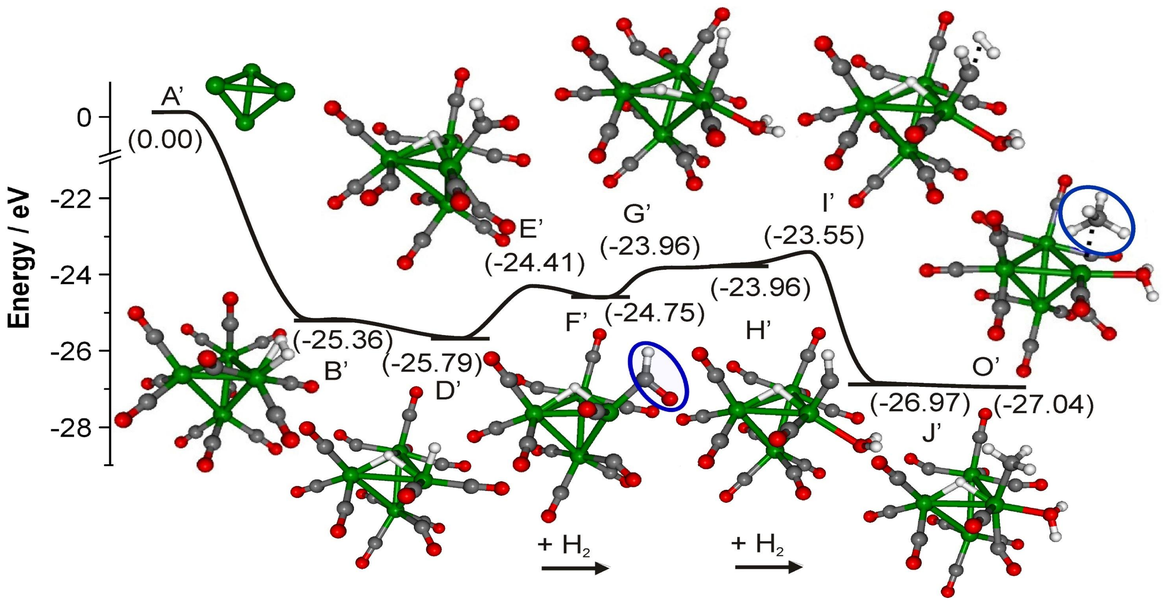

(c) $D_2$ ligand fraction (average number of $D_2$ molecules normalized to the total number of ligands in all observed complexes $Ru_4(CO)_{14-m}D_{2m+1}^+$ and $Ru_6(CO)_{18-m}D_{2m}^+$, respectively) as a function of the $CO/D_2$ partial pressure ratio. Next to each data point the numbers *m* of the observed coadsorption products are given. The solid lines are drawn to guide the eye [4].

← Product mass spectra obtained after reaction of (a) $Ru_4^+$ and (b) $Ru_6^+$ with a 1:100 mixture of CO and $D_2$. The corresponding DFT structures of the most abundant products are also shown. Ru, C, O and H are indicated by green, gray, red, and white spheres, respectively [4].

## CO Methanation Reaction Mechanism




Calculated energy profile and corresponding structures for CO methanation by reaction of one CO with four sequentially adsorbed $H_2$ molecules mediated by $Ru_6^+$ (doublet ground state). The solid black line labels the pathway involving the formyl-type intermediate, whereas the gray dashed line labels the first step of the alternative CO bond breaking pathway. The blue circles highlight the formyl-type intermediate in structure F and the final methane product in structure O. The numbers denote the relative energies of the local minima and transition states in eV [4].




Calculated energy profile for CO methanation by reaction of the hydrido carbonyl $Ru_4(CO)_{13}H_2^+$ (doublet ground state) with two sequentially adsorbed $H_2$ molecules together with the corresponding structures. The numbers indicate the relative energies in eV. The blue circles highlight the formyl-type intermediate in structure F' and the final methane product in structure O' [4].

## References

[1] L. Carrette, K. A. Friedrich, U. Stimming, *Chem. Phys. Chem.* **2000**, *1*, 162.
[2] S. Eckle, M. Augustin, H.-G. Anfang, R. J. Behm, *Catal. Today* **2012**, *181*, 40.
[3] S. M. Lang, S. U. Förtig, T. M. Bernhardt, M. Krstić, V. Bonačić-Koutecký, *J. Phys. Chem. A*. **2014**, DOI: 10.1021/jp501242c.
[4] S. M. Lang, T. M. Bernhardt, M. Krstić, V. Bonačić-Koutecký, *Angew. Chem. Int. Ed.* **2014**, in press.