DOI: 10.1002/anie.201310134

CO Methanation

The Origin of the Selectivity and Activity of Ruthenium-Cluster Catalysts for Fuel-Cell Feed-Gas Purification: A Gas-Phase Approach[**]

Sandra M. Lang, Thorsten M. Bernhardt,[*] Marjan Krstić, and Vlasta Bonačić-Koutecký[*]

Abstract: *Gas-phase ruthenium clusters* Ru_n^+ *(*$n = 2$*–*6*) are employed as model systems to discover the origin of the outstanding performance of supported sub-nanometer ruthenium particles in the catalytic CO methanation reaction with relevance to the hydrogen feed-gas purification for advanced fuel-cell applications. Using ion-trap mass spectrometry in conjunction with first-principles density functional theory calculations three fundamental properties of these clusters are identified which determine the selectivity and catalytic activity: high reactivity toward CO in contrast to inertness in the reaction with* CO_2*; promotion of cooperatively enhanced* H_2 *coadsorption and dissociation on pre-formed ruthenium carbonyl clusters, that is, no CO poisoning occurs; and the presence of Ru-atom sites with a low number of metal–metal bonds, 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.*

The electrochemical energy conversion is one of the key technologies for the 21st century. In particular the direct conversion of chemical into electrical energy has received utmost attention because of its potential for a "green" environmentally compatible technology. This conversion is realized in fuel cells, in which the energy released by the reaction of hydrogen and oxygen through an electrocatalytic process is directly converted into electricity.[1,2]

With respect to applications in transportation and decentralized small-scale appliances in particular the low-temperature proton-exchange membrane fuel cell (PEMFC) has gained increasing importance.[2] Often, the hydrogen feed gas for PEMFCs is generated by reformation of fossil fuels[3] (e.g., methane) which, however, results in the formation of CO as an undesired byproduct. Subsequent energy conversion in the PEMFC is catalyzed by metal particles (often platinum or platinum alloys) which are poisoned by even small amounts of CO. Thus, the development of cost-efficient techniques to improve the feed-gas quality (minimization of the CO fraction) represents an important research field.

One promising procedure for CO removal is the catalytic reaction with hydrogen to form CH_4 and water (methanation). However, feed gases usually also contain about 10 %[4] of CO_2 which can react catalytically with H_2 to form CH_4 (methanation) or CO (reverse water–gas shift reaction). This process either leads to a non-tolerable loss of hydrogen or to the production of additional CO. Thus, selective CO methanation to minimize CO poisoning of the fuel cell anode is essential for the future viability of the PEMFCs.[5] For this purpose oxide-supported ruthenium particle catalysts have been shown to be very promising materials.[6] The high activity and selectivity of these catalysts was traced in particular to the presence of very small Ru clusters (< 1 nm).[7] However, the reason why small ruthenium clusters are active and selective for fuel-cell feed-gas purification remains an open question.

Herein, gas-phase ruthenium clusters Ru_n^+ ($n = 2$–6) are employed as model systems to discover the origin of the outstanding performance of supported sub-nanometer ruthenium particles in the catalytic CO methanation reaction. Positively charged clusters have been chosen because previous experiments with supported clusters could show a partial positive charging of Ru particles on oxide supports.[6,8] Using ion-trap mass spectrometry in conjunction with first-principles density functional theory (DFT) calculations three fundamental properties of these clusters are identified which determine the selectivity and catalytic activity: a) high reactivity toward CO in contrast to inertness in the reaction with CO_2; b) promotion of cooperatively enhanced H_2 coadsorption and dissociation on pre-formed ruthenium carbonyl clusters, that is, no CO poisoning occurs; and c) the presence of Ru-atom sites forming a low number of metal–metal bonds, 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.

In the following we will first address the origin of the CO/CO_2 selectivity: In a first series of experiments the reaction of Ru_n^+ ($n = 2$–6) with several typical components of a fuel-cell feed gas,[4,9] such as CO_2, CO, H_2, CH_4, and N_2 have been investigated independently. The clusters were found to

---

[*] Dr. S. M. Lang, Prof. Dr. T. M. Bernhardt
Institute of Surface Chemistry and Catalysis, University of Ulm
Albert-Einstein-Allee 47, 89069 Ulm (Germany)
E-mail: thorsten.bernhardt@uni-ulm.de

M. Krstić, Prof. Dr. V. Bonačić-Koutecký
Interdisciplinary Center for Advanced Sciences and Technology (ICAST), University of Split
Meštrovićevo Šetalište 45, 21000 Split (Croatia)

Prof. Dr. V. Bonačić-Koutecký
Chemistry Department, Humboldt University of Berlin
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
E-mail: vbk@chemie.hu-berlin.de

[**] This work was supported by the DAAD and the FCI. S.M.L. is grateful to the ESF Baden-Württemberg for a Margarete von Wrangell fellowship. We thank Sandra Förtig for experimental assistance and Prof. R. Jürgen Behm for stimulating discussions.

strongly react with CO, while being completely non-reactive toward CO_2 in agreement with the calculated CO and CO_2 binding energies (e.g., $E_b(Ru_4^+–CO) = 1.76$ eV vs. $E_b(Ru_4^+–CO_2) = 0.45$ eV). This already explains why small ruthenium clusters are highly selective in catalyzing the methanation of CO whilst preventing concurrent unwanted hydrogen consuming CO_2 conversion.

In fact, the strong binding of CO to ruthenium results in the formation of ruthenium carbonyl complexes as apparent from the product mass spectra obtained after the reaction of Ru_4^+ and Ru_6^+ with CO shown in Figure 1 a,b. These reactions are very fast (faster than the time resolution of the experiment which amounts to about 0.1 s) and yield only one single reaction product each.[10] The exclusive appearance of $Ru_4(CO)_{14}^+$ and $Ru_6(CO)_{18}^+$ (and $Ru_5(CO)_{16}^+$, not shown)[11] in the ion-trap reaction mass spectra under all reaction conditions points toward their pronounced stability, which can be explained by a closed-shell-type 18 valence electron count for each metal atom center.[10,12] The geometries of these closed-shell configurations were revealed by first principles DFT calculations and are depicted in Figure 1 a,b.[10]

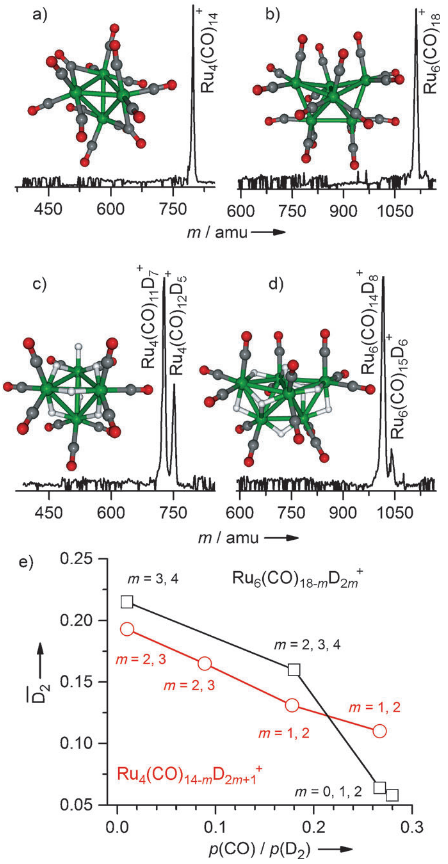

Figure 1. Product mass spectra obtained after reaction of a) Ru_4^+ and b) Ru_6^+ with CO as well of c) Ru_4^+ and d) Ru_6^+ with a 1:100 mixture of CO and D_2 for $t_R = 0.1$ s. Also displayed are the corresponding DFT structures of the most abundant products. Ru green, C gray, O red and H white spheres. e) D_2 ligand fraction $\bar{D}_2$ (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 to guide the eye.

All the ruthenium clusters were non-reactive with nitrogen and methane, which are both present at high abundance in the fuel-cell feed gas (only Ru_2^+ yielded $Ru_2CD_2^+$). Furthermore, in the presence of hydrogen (D_2) Ru_4^+ and Ru_6^+ were the only clusters found to yield reaction products ($Ru_4D_4^+$ and $Ru_6D_2^+$, respectively). Overall, the exceptional reactive behavior of the small Ru clusters toward CO (in contrast to CO_2, which was found not to react under any reaction conditions) and the formation of the stable carbonyl complexes provide the basis for the understanding of the observed CO methanation selectivity and the pertinent size effect.

Now we will turn to the origin of the activity of the small Ru clusters focusing on cooperative coadsorption effects and adsorption site dependent hydrogen dissociation: In a second series of gas-phase experiments the coadsorption of CO and D_2 has been investigated. If a mixture of CO and D_2 is introduced into the ion trap, Ru_4^+ and Ru_6^+ form complexes containing both molecules as can be seen from the mass spectra in Figure 1 c,d. This finding is particularly important since it demonstrates that in spite of the high calculated CO binding energies ($E_b(Ru_4^+–CO) = 1.76$ eV vs. $E_b(Ru_4^+–H_2) = 0.66$ eV and $E_b(Ru_6^+–CO) = 1.69$ eV vs. $E_b(Ru_6^+–H_2) = 0.59$ eV) the coadsorption of hydrogen is possible and CO poisoning does not occur.

On the contrary, CO even actively promotes the hydrogen coadsorption because the observed complex $Ru_4(CO)_{11}D_7^+$ (Figure 1 c) contains seven hydrogen (deuterium) atoms while with only hydrogen present in the ion trap at most four D ligands are adsorbed. This cooperative coadsorption is even more pronounced for Ru_6^+ which coadsorbs up to eight D atoms ($Ru_6(CO)_{14}D_8^+$ in Figure 1 d). In contrast, the adsorption of only two D atoms is observed in the presence of exclusively hydrogen in the ion trap.

Even more insight into the origin of this cooperative effect of CO pre-adsorption on the subsequent D_2 coadsorption is provided by our theoretical results. From the calculated structures shown in Figure 1 c,d it is clear that hydrogen is dissociatively bound in the hydrido carbonyl complexes. In addition, the dissociation of a single hydrogen molecule has been calculated to be 0.2 eV more exothermic in the presence of a CO molecule adsorbed on the same Ru center than without pre-adsorbed CO. This result illustrates that the presence of the pre-adsorbed CO supports the hydrogen dissociation which is the essential prerequisite for the subsequent methanation reaction via formyl formation.

Figure 1 e illustrates that these cooperative effects prevail at high CO partial pressures. This graph displays the detected hydrido carbonyl complex compositions as a function of the CO to D_2 partial-pressure ratio. Even at the highest investigated CO contents (28 %) the coadsorption of hydrogen is still observed (technically employed fuel-cell feed gases contain only up to about 8 mol % of CO[4]). All the observed hydrido carbonyl complexes exhibit the stoichiometries $Ru_4(CO)_{14-m}D_{2m+1}^+$ and $Ru_6(CO)_{18-m}D_{2m}^+$, respectively, in which the total number of ligands remains unchanged, while the number m of coadsorbed hydrogen molecules varies with the applied CO/D_2 pressure ratio. Hence, the 18 valence electron count for each Ru atom is preserved.[10] The odd number of D atoms in $Ru_4(CO)_{14-m}D_{2m+1}^+$ can be explained by the fact that the additional D atom in this case now balances the positive charge which had been neglected above in the original valence electron count.[10]

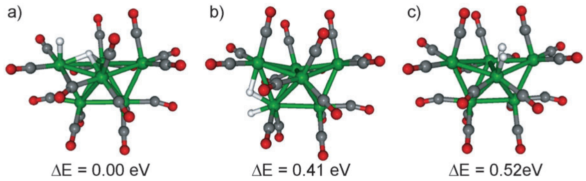

Figure 2. Optimized structures of $Ru_6(CO)_{17}H_2^+$ comprising H_2 adsorbed at a Ru atom bound to a) three, b) four, and c) five other Ru atoms.

To further elucidate the high activity of the small ruthenium clusters, the preferred adsorption site of H_2 in the carbonyl cluster complexes was analyzed. In the tetrahedral Ru_4^+ all the Ru atoms are equivalent and each forms three Ru–Ru bonds and our DFT studies reveal that H_2 adsorbs dissociatively on the Ru_4^+ carbonyl cluster (Figure 1 c). In contrast, the bicapped tetrahedral Ru_6^+ cluster also contains Ru atoms involved in four or five Ru–Ru bonds as well as those bound to three other ruthenium centers. Figure 2 shows that in the energetically lowest structure of $Ru_6(CO)_{17}H_2^+$ (Figure 2 a) the hydrogen is bound dissociatively to a Ru atom bound to three other Ru centers. The binding of hydrogen to Ru atoms with more metal–metal bonds is considerably less favorable (Figure 2 b and c).

Hence, Ru atoms with a low number of metal–metal bonds present the centers of highest activity in the first step of the methanation reaction. In terms of numbers of metal–metal bonds such a coordination environment resembles that of low-coordinate metal atoms on bulk metal surfaces. Such sites are most abundant in very small particles, thus, representing in addition to the cooperative effects the origin of the high activity of small ruthenium clusters.

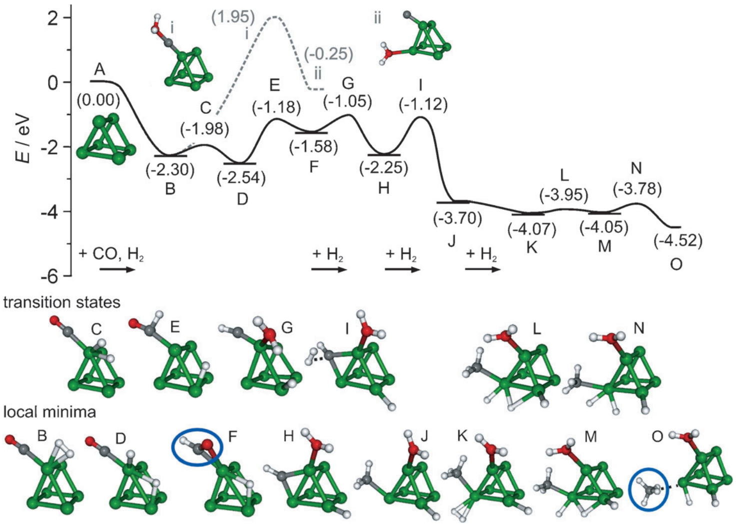

Figure 3. Calculated energy profile and corresponding structures for CO methanation by reaction of one CO with four sequentially adsorbed H_2 molecules mediated by Ru_6^+ (doublet ground state). The solid black line labels the pathway involving the formyl-type intermediate, whereas the gray dashed line 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.

Finally, we employ first-principles DFT calculations to reveal the CO methanation reaction mechanism. We first focus on the reaction of Ru_6^+. This bare cluster exhibits a trigonal prismatic structure comprising only equivalent atoms bound to three other metal centers (cf. structure A in Figure 3), which we found to be particularly reactive above. Therefore, it serves as a good model for the reaction study in which CO and H_2 are coadsorbed at the same Ru atom of this cluster (structure B in Figure 3). Starting from this species two fundamentally different reaction pathways can be envisaged: 1) The hydration of the carbon atom and 2) the hydration of the oxygen atom of CO. The first pathway involves the formation of a formyl-type reaction intermediate and is identified herein to be the energetically most favorable mechanism (black line in Figure 3). In contrast, the second pathway proceeds by C–O bond breaking and is unfeasible because the energy barrier involved considerably exceeds the binding energies of CO and H_2, respectively (dashed line in Figure 3). Therefore only pathway (1) is considered in the following.

The dissociation of H_2 involves only a small barrier (as discussed above) and leads to structure D. The subsequent formyl (HCO) formation (structure F) proceeds across an activation barrier of 1.36 eV, which is associated with the transfer of hydrogen to the carbon atom (D→E→F), and overall is exothermic by 1.58 eV. Notice that for the reaction with neutral clusters the corresponding activation barrier is only slightly higher (by 0.2 eV) which illustrates that the charge of the complexes is not decisive for the formyl formation. However the slightly more favorable path with charged clusters is in very good agreement with the partial positive charge observed for the highly active Ru particles on oxide supports.[6,8]

By adding a second hydrogen molecule, the formation of a water molecule and a methyne (CH) ligand at the same Ru atom (structure G) occurs (F→G→H). The adsorption of two more H_2 molecules is required to accomplish the formation of CH_4 which is finally liberated to yield structure O in Figure 3. The overall methanation reaction is exothermic by 4.52 eV and the calculated barriers are substantially lower than the initial energy. Furthermore, the discovery of a reaction mechanism proceeding via formation of a formyl-type intermediate is in favorable agreement with in situ IR spectroscopic studies which unambiguously identified

HCO_{ad} as the intermediate in the CO methanation mediated by Ru/Al_2O_3 catalysts.[13]

To build the link from the simplified model system (Ru_6^+ with one CO and four sequentially adsorbed H_2, Figure 3) to the experimentally observed CO-rich complexes, the energy profile for the methanation reaction starting from the hydrido carbonyl complex $Ru_4(CO)_{13}H_2^+$ has been calculated as shown in Figure 4. The reaction proceeds along a mechanistically and energetically very similar pathway involving a formyl-type intermediate. In particular, the main activation barrier associated with the formation of the formyl-type intermediate F′ (1.38 eV) is identical to the barrier in case of Ru_6^+ (1.36 eV). In contrast, the subsequent barrier for water formation is slightly increased while, however, the barrier for methyne hydrogenation is considerably decreased in the presence of multiple CO molecules. Furthermore it is interesting to note that the increased number of CO molecules leads to the disappearance of the activation barrier for the dissociation of the first H_2 molecule and to the stabilization of the dissociated hydrogen. This observation is in agreement with the discussion above.

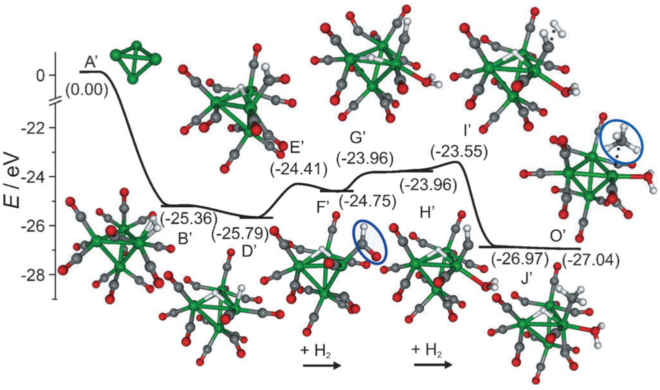

Figure 4. Calculated energy profile for CO methanation by reaction of the hydrido carbonyl $Ru_4(CO)_{13}H_2^+$ (doublet ground state) with two sequentially adsorbed H_2 molecules shown together with the corresponding structures. The numbers indicate the relative energies in eV. The blue circles highlight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

All of the calculated activation barriers are smaller than 1.4 eV and thus can be easily surmounted at room temperature under the reaction conditions of our ion-trap experiment as previously shown.[14] Indeed, all the reaction products are in equilibrium in the ion-trap experiment (the intensities in Figure 1 c,d do not change with increasing reaction time) which supports the occurrence of the catalytic CO methanation reaction cycle. The neutral reaction products of the catalytic cycle (CH_4 and H_2O, see Figure 3 and Figure 4) have been shown theoretically and experimentally to only very weakly bind to the Ru clusters. Thus, once formed they will be immediately released and instantly CO and H_2 adsorption will occur again closing the reaction cycle and leading to the observed equilibrium reaction products.

It is important to emphasize that the reactions in the ion trap proceed in thermal equilibrium, thus, the formyl-type intermediate mechanism is operative. In contrast, in additional, separate non-thermal collision-induced activation experiments the C–O bond cleavage could be observed at high impact energies thus confirming the considerably higher calculated activation barrier for this mechanism as shown in Figure 3.

Herein we have presented a joint experimental and theoretical gas-phase investigation that aims at elucidating the origin of the outstanding catalytic selectivity and activity of small ruthenium clusters in the CO methanation reaction. These model studies can be considered as an important step toward a conceptual mechanistic understanding of the recently discovered excellent performance of oxide-supported Ru particle catalysts employed for fuel-cell feed-gas purification. Moreover, these conceptual insights also open a new avenue for transferring model system results to guide the design strategies for catalytic materials for fuel-cell feed-gas purification. Hence, improved supported methanation catalysts should have the following properties: a) high reactivity toward CO (precondition for CO/CO_2 selectivity), b) yet, promoting hydrogen coadsorption, and c) clusters with Ru atom sites with few metal–metal bonds, which facilitate the methanation reaction via formyl intermediate formation. Apparently, only catalysts containing very small Ru clusters will satisfy all three of these conditions. Therefore, we wish to propose to employ intrazeolite anchored Ru carbonyl and hydridocarbonyl complexes, in particular $Ru_6(CO)_{18}$ as well as $H_4Ru_4(CO)_{12}$, which have been synthesized in the condensed phase previously,[15] as a new catalytic system for fuel-cell feed-gas purification by methanation of CO. Work is in progress in our laboratories in this direction.

Experimental Section

Experimental Method: Gas-phase ruthenium clusters are prepared by sputtering of Ru metal targets with high energy Xe ion beams. The produced clusters are mass selected in a first quadrupole mass filter and are subsequently guided into the home-built radio frequency octopole ion trap, which is pre-filled with 1–2 Pa of helium buffer gas and 0.002–0.1 Pa partial pressures of the reactant molecules.[16] During the experiments the ion trap is held at room temperature and after a chosen reaction time, that is, storage time inside the ion trap, all ions, products, and intermediates, are extracted and mass analyzed by a second quadrupole mass filter. Throughout these experiments deuterium and deuterated methane was employed to facilitate the mass assignment.

Theoretical Method: The structural properties of the ruthenium cluster cations and their reactivity were studied using DFT with the hybrid B3LYP functional.[17] For the Ru atoms the Stuttgart group relativistic effective core potentials (ECPs)[18] were employed together with the triple-ζ-valence-plus-polarization basis sets which was also used for the C, O, and H atoms.[19] Our previous studies of the reactivity of transition-metal clusters and oxide clusters have shown that such a combination of hybrid density functionals with triple-ζ quality basis sets allows the accurate prediction of the reaction energetics and mechanisms.[20] All structures presented were fully optimized using gradient minimization techniques and stationary points were characterized as minima or transition states by calculating the vibrational frequencies. Moreover, from the energy profiles based on energies obtained from DFT calculations the reaction mechanisms were deduced. To improve efficiency for the larger carbonyl complexes and their reactivity, the resolution of identity (RI)-DFT procedure[21] has been employed using the Perdew-Burke-Ernzerhof functional with the same ECPs and basis sets.[22] The accuracy of this functional has been checked through comparison with the results obtained by the B3LYP functional for the $Ru_4(CO)_{14}^+$ complex.

Received: November 21, 2013
Revised: February 4, 2014

Keywords: ab initio calculations · heterogeneous catalysis · CO methanation · mass spectrometry · ruthenium clusters

---

[1] S. Srinivasan, R. Mosdale, P. Stevens, C. Yang, *Ann. Rev. Energy Environ.* **1999**, *24*, 281 – 328.

[2] L. Carrette, K. A. Friedrich, U. Stimmig, *ChemPhysChem* **2000**, *1*, 162 – 193.

[3] D. L. Trimm, Z. I. Önsan, *Catal. Rev.* **2001**, *43*, 31 – 84.

[4] D. L. Trimm, *Appl. Catal. A* **2005**, *296*, 1 – 11.

[5] A. Mishra, R. Prasad, *Bull. Chem. React. Eng. Catal.* **2011**, *6*, 1 – 14.

[6] S. Eckle, Y. Denkwitz, R. J. Behm, *J. Catal.* **2010**, *269*, 255 – 268.

[7] a) S. Tada, R. Kikuchi, K. Urasaki, S. Satokawa, *Appl. Catal. A* **2011**, *404*, 149 – 154; b) S. Eckle, M. Augustin, H.-G. Anfang, R. J. Behm, *Catal. Today* **2012**, *181*, 40 – 51.

[8] S. Scirè, C. Crisafulli, R. Maggiore, S. Minicò, S. Galvagno, *Catal. Lett.* **1998**, *51*, 41 – 45.

[9] W. Ruettinger, O. Ilinich, R. J. Farrauto, *J. Power Sources* **2003**, *118*, 61 – 65.

[10] S. M. Lang, S. U. Förtig, T. M. Bernhardt, M. Krstić, V. Bonačić-Koutecký, *J. Phys. Chem. A* **2014**, DOI: 10.1021/jp501242c.

[11] In the case of Ru_2^+ and Ru_3^+ the reaction with CO leads to fragmentation of these species (to yield Ru^+) because the Ru–Ru binding energy is smaller than the CO adsorption energy.

[12] a) N. Sidgwick V, *Trans. Faraday Soc.* **1923**, *19*, 469 – 475; b) N. Sidgwick V, R. W. Bailey, *Proc. R. Soc. London Ser. A* **1934**, *144*, 521 – 537.

[13] S. Eckle, H.-G. Anfang, R. J. Behm, *J. Phys. Chem. C* **2011**, *115*, 1361 – 1367.

[14] S. M. Lang, T. M. Bernhardt, R. N. Barnett, U. Landman, *Angew. Chem.* **2010**, *122*, 993 – 996; *Angew. Chem. Int. Ed.* **2010**, *49*, 980 – 983.

[15] J. G. C. Shen, A. M. Liu, T. Tanaka, M. Ichikawa, *J. Phys. Chem. B* **1998**, *102*, 7782 – 7792.

[16] T. M. Bernhardt, *Int. J. Mass Spectrom.* **2005**, *243*, 1 – 29.

[17] a) A. D. Becke, *Phys. Rev.* **1988**, *38*, 3098 – 3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[18] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123 – 141.

[19] A. Schäfer, H. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829 – 5835.

[20] a) G. E. Johnson, R. Mitric, V. Bonacic-Kouteckeý, A. W. Castleman, Jr., *Chem. Phys. Lett.* **2009**, *475*, 1 – 9; b) D. R. Justes, R. Mitrić, N. A. Moore, V. Bonačić-Koutecký, A. W. Castelman, Jr., *J. Am. Chem. Soc.* **2003**, *125*, 6289 – 6299; c) G. E. Johnson, R. Mitric, M. Nössler, E. C. Tyo, V. Bonacic-Kouteckeý, A. W. Castleman, Jr., *J. Am. Chem. Soc.* **2009**, *131*, 5460 – 5470.

[21] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283 – 290.

[22] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865 – 3868.