Direct hot-carrier transfer in plasmonic catalysis

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Abstract

Plasmonic metal nanoparticles can concentrate optical energy and enable chemical reactions on their surfaces. The interaction of plasmon with the adsorbate orbitals leads to plasmon-induced hot-carrier transfer to the adsorbate, leading to chemical transformations. The hot-carrier transfer is known to occur via two pathways: (i) *indirect transfer*, where the hot carriers are first produced in the metal and are then transferred to the adsorbate, and (ii) *direct transfer*, where the plasmons decay by directly exciting a carrier from the metal to the adsorbate. Unfortunately, the atomic-level details and knowledge of the efficiency of this direct-transfer process are missing. Here, we report a preliminary investigation employing time-dependent density-functional theory (TDDFT) calculations to capture and quantify the direct-transfer process at a model metal–adsorbate (Ag₁₄₇-CO) interface. For a 10-femtosecond Gaussian laser pulse tuned to the plasmon frequency, we observe a plasmon-induced direct hot-electron transfer process arising from the occupied states of Ag to the unoccupied molecular orbitals of CO. Our work provides evidence for the direct-transfer process at Ag-CO interfaces and shows that the efficiency of the direct-transfer process depends on the adsorption site. We envision our computations to provide theoretical guidelines to design more efficient metal-molecule interfaces for plasmonic catalysis.

Introduction

Plasmonic photocatalysis aims to carry out chemical reactions directly on the surface of a plasmonic-metal nanoparticle efficiently and selectively.¹⁻⁵ This approach exploits the properties of localized surface plasmons (LSPs), which are collective charge density oscillations induced in a plasmonic-metal nanoparticle upon interaction with light. Over time, the LSP decays to generate energetic charge carriers (referred to as hot electrons and hot holes). The resulting electrons can get transferred to the unoccupied molecular orbitals of the adsorbate, resulting in the formation of a transient negative ion complex. Because the absorbate is pushed to a different potential energy surface, forces are induced on the adsorbate nuclei. This causes the atoms to move, thus triggering chemical transformations on the surface of a plasmonic metal.²

Plasmonic catalysis is advantageous in many ways. Because LSPs can concentrate light and enhance optical energy absorption, they can increase the concentration of hot carriers leading to improved external quantum efficiency (EQE).⁶ This provides a platform to utilize low-intensity sunlight as a renewable source of energy.⁷ In addition, being fundamentally different from thermal catalysis in terms of mechanism, they could enable new reaction outcomes and help engineer product selectivity.⁴

In plasmonic catalysis, the hot-carrier transfer process represents a critical step. It can occur via two mechanisms:^{2,3,8-11} (i) *indirect transfer*, where the hot carriers are first produced in the metal nanoparticle, and eventually transferred to the acceptor (Fig. 1a), or (ii) *direct transfer* (or *chemical interface damping*^{12,13}), where the plasmon decays by directly exciting an electron from the occupied states of the metal to the unoccupied orbitals of the adsorbate (*direct hot-electron transfer*, Fig. 1b). The plasmons can also decay by directly exciting an electron from the occupied states of the adsorbate to the unoccupied of the metal, a transition that leads to a *direct hot-hole transfer* to the adsorbate. Because the hot carriers generated in the metal can quickly relax back to the Fermi level via carrier–carrier interactions before they are transferred to the adsorbate, studies have constantly pointed out that the indirect-transfer process can be inefficient.¹⁴⁻¹⁷ On the other hand, this problem can be avoided in the direct-transfer process.¹⁴ As such, controlling and favoring the direct-transfer process at the expense of the indirect-transfer process could potentially lead to higher EQEs.

However, plasmonic catalysis continues to suffer from poor EQEs (less than 1%) and poor control over product selectivity.^{2,18,19} This is because although the direct-transfer process is known to be more efficient, it has been poorly understood at the atomic scale. As a result, no significant efforts have been made to discover ways to promote this process and tap its potential for plasmonic catalysis.

Here, we report a preliminary *ab initio* investigation based on real-time time-dependent density-functional theory (RT-TDDFT²⁰) to capture and study the direct-transfer process at a model metal–adsorbate interface formed by a metallic Ag₁₄₇ nanoparticle and a CO molecule. The rationale for choosing a computational approach comes from the fact that the two hot-carrier transfer processes occur simultaneously, and isolating individual processes in experiments can be a daunting task. Furthermore, since these processes occur on ultrafast timescales (1 fs – 100 ps),^{8,10} interface-design to promote the direct-transfer process via experiments can be complicated and time-consuming.

We demonstrate that the plasmon formed in the Ag₁₄₇-CO system due to an applied laser pulse induces a direct hot-electron transfer from the occupied states of Ag to the unoccupied molecular orbitals of CO. We study three adsorption configurations of CO: on-top, bridge and hollow adsorption sites. We find the efficiency of the direct hot-electron transfer process to be 0.86, 1.96 and 1.78%, respectively, showing that the direct-transfer process can be tuned depending on the adsorption configuration of a molecule. We also evidence the direct hot-hole transfer process in these configurations, albeit with much smaller efficiency values. Overall, our study provides an approach to capture and quantify the direct-transfer process at a given metal-molecule interface. It also provides a framework for rational metal-molecule interface design for plasmonic catalysis.

Methods

The Ag₁₄₇-CO interface models used in our study, with CO adsorbed at three different sites (on-top, bridge and hollow), are shown in Fig. 2. The interface normal for all the three configurations lies along the x-axis. The icosahedral Ag₁₄₇ nanoparticle previously studied by Kuisma *et al.*²¹ and Rossi *et al.*²² is known to support a strong plasmon. Because previous experiments have investigated selective oxidation of CO directly on plasmonic Ag nanoparticles, we chose the CO molecule as a model adsorbate in our study.^{6,23} First, the Ag₁₄₇ and CO structures are relaxed individually to less than 0.03 eV/Å residual forces at the DFT level of theory^{24,25} using the GPAW code.^{26,27} A grid spacing of 0.3 Å, and a vacuum spacing of 12 Å is used in our calculations. The Ag₁₄₇-CO combined structures are then formed and relaxed to less than 0.03 eV/Å residual forces. During this relaxation step, the atoms of the Ag₁₄₇ nanoparticle are fixed, while CO molecule is allowed to relax.

We use the projector augmented-wave (PAW) method to describe the core electrons,²⁸ and the Perdew-Burke- Ernzerhof (PBE) exchange-correlation (xc) functional²⁹ in relaxation calculations. The wavefunctions are represented using a linear combination of atomic orbitals (LCAO).³⁰ We use the default double- ζ polarized (DZP) basis set for geometry relaxation and include 11, 4, and 6 valence electrons to model Ag, C, and O atoms, respectively.³¹

The optical properties are computed using the LCAO-RT-TDDFT method as implemented in GPAW.^{21,22} We replace the standard p-type polarization function of the Ag atom with the actual Kohn-Sham orbital of the 5p state plus its usual split-valence function, which is known to describe plasmons accurately in Ag nanoparticles.²¹ We employ the orbital-dependent GLLB-SC xc potential.³² A Fermi-Dirac smearing of 0.05 eV is used to facilitate the convergence with the used xc potential. More details on the methodology are given in Ref. 22.

Results and Discussion

The plasmon resonances are determined by computing the photoabsorption spectra using the δ -kick technique.³³ The electric field in these calculations is applied along the x-axis. Fig. 3a shows the results for individual Ag₁₄₇ and CO systems, as well as for the three different adsorption configurations considered. A Gaussian broadening of 0.2 eV full-width at half maximum was

applied to the spectra. We observe a strong plasmon peak at 3.71 eV for Ag_{147} , which is consistent with previous calculations.²² As expected, given a computed HOMO-LUMO gap value of 7.9 eV, CO does not show any photoabsorption in the energy range plotted. For the Ag_{147} -CO systems, the adsorption of CO causes only a small change in the plasmon peak position, moving it to 3.74 eV.

To study hot-carrier generation and transfer at the three Ag₁₄₇-CO interfaces, we excite the systems along the x-axis with a laser pulse at the plasmon frequency. The external electric field takes on the form $\mathbf{E}(t) = \mathbf{E}_0 \sin(\omega_p(t - t_0)) \exp(-\sigma^2 (t - t_0)^2/2)$, where *t* represents time, \mathbf{E}_0 is the field intensity (assumed to be weak to probe the linear response regime), t_0 is the pulse peak time (set to 10 fs), ω_p is the pulse frequency (set to plasmon frequency 3.74 eV), and σ describes the pulse width (set to a value corresponding to pulse duration of ~10 fs).

The applied laser pulse and the dipole-moment response of the Ag₁₄₇-CO (on-top configuration) system as a function of time is shown in Fig. 3b. The pulse is turned on at ~5 fs, reaches a maximum at 10 fs, and fades away after 15 fs. In response to this field, it is seen that the dipole moment shows large amplitude oscillations, reaching a maximum at ~12 fs and decays to a steady minimum value beyond 27 fs. The dipole moment continues to persist even after the pulse is turned off, which is suggestive of a resonant excitation of the plasmonic system.¹⁷

We further investigate the formation of a plasmon by visualizing the induced charge density in real space at 12 and 27 fs, as shown in Fig. 3c. The charge density at 12 fs clearly shows collective motion of charges from one side of the metal nanoparticle to the other, which is a clear indication of a plasmon mode excitation. At later times (27 fs), we note that the charge-density distribution loses the collective oscillatory behavior and becomes mostly fragmented. This suggests that the plasmon formed at 12 fs has decayed, and hot carriers are generated in the system.

We compute the resulting hot-carrier distribution at a given time t using the transition probability $P_{ia}(t) = \left|\delta\rho_{ia}^{x}(t)/\sqrt{(f_{i}-f_{a})}\right|^{2}$, where the Kohn-Sham (KS) transition density matrix, $\delta\rho_{ia}^{x}(t) = \rho_{ia}^{x}(t) - \rho_{ia}(0)$, is constructed in the basis of occupied (i) and unoccupied (a) KS states, and f_i and f_a are the ground-state occupations of the KS states *i* and *a*, respectively.³⁴ Specifically, the probabilities for creating an electron on state *a*, and a hole on state *i* are given by $P_a(t) = \sum_i P_{ia}(t)$ and $P_i(t) = \sum_a P_{ia}(t)$, respectively.³⁴ The corresponding hot-electron distribution $P_e(E, t)$ presents the occupation probability with respect to the eigenvalues of the states, $P_e(E, t) = \sum_a P_a(t) \mathcal{G}_a(E)$, where a Gaussian broadening function is employed. The hothole distribution $P_h(E, t)$ is computed analogously.

Fig. 3d shows the total hot-carrier distribution, P_{hc} , in the three Ag₁₄₇-CO systems at 27 fs, *i.e.* after the plasmon has decayed. We observe that a large concentration of holes is generated at around -4 eV, consequently generating a large concentration of electrons close to the Fermi level. This is attributed to the interband $(d \rightarrow sp)$ transitions commonly observed in Ag nanoparticles. The hot-hole and hot-electron distributions at other energy levels arise due to the intraband $(sp \rightarrow sp)$ transitions in the Ag nanoparticle, and additional transitions that occur across the Ag-CO interface (which constitute the direct-transfer process).

The total hot-carrier distribution, P_{hc} , can be divided into four partial transitions: (i) $P_{hc}^{Ag \rightarrow Ag}$, from the occupied states of Ag to the unoccupied states of Ag, (ii) $P_{hc}^{CO\rightarrow CO}$, from the occupied states of CO to the unoccupied states of CO, (iii) $P_{hc}^{Ag\rightarrow CO}$, from the occupied states of Ag to the unoccupied states of CO, and (iv) $P_{hc}^{CO\rightarrow Ag}$, from the occupied states of CO to the unoccupied states of Ag. Therefore, $P_{hc} = P_{hc}^{Ag\rightarrow Ag} + P_{hc}^{CO\rightarrow CO} + P_{hc}^{Ag\rightarrow CO} + P_{hc}^{CO\rightarrow Ag}$. Here, $P_{hc}^{Ag\rightarrow Ag}$ relates to the indirect-transfer process, where the hot carriers are first generated within the Ag nanoparticle and subsequently move to CO. $P_{hc}^{CO\rightarrow CO}$ is commonly referred to as *intra-adsorbate excitation*,^{23,35} which is found to be negligible in the present case. The partial transitions, $P_{hc}^{Ag\rightarrow CO}$ and $P_{hc}^{CO\rightarrow Ag}$, constitute the direct hot-electron and the direct hot-hole transfer, respectively.

To capture the direct-transfer process, we divide the simulation cell into two complementary spatial regions determined by the boundary between Ag and CO atoms. For each KS state *n*, Ag and CO weights are then calculated from the ground-state KS wave function $\Psi_n(\mathbf{r})$ as $w_n^{Ag} = \int_{\mathbf{r} \in Ag} |\Psi_n(\mathbf{r})|^2 d\mathbf{r}$, and $w_n^{CO} = \int_{\mathbf{r} \in CO} |\Psi_n(\mathbf{r})|^2 d\mathbf{r}$, respectively, satisfying $w_n^{Ag} + w_n^{CO} = 1$.

Then, the partial hot-carrier distributions are obtained by using the weights for occupied (*i*) and unoccupied (*a*) states in the transition probability. For example, the direct hot-electron transition, $P_{hc}^{Ag \rightarrow CO}$ distribution is obtained by using the weighted transition density $P_{ia}^{Ag \rightarrow CO}(t) = \Psi_i^{Ag} \cdot \Psi_a^{CO} \cdot P_{ia}(t)$. Then, the expression $P_a^{Ag \rightarrow CO}(t) = \sum_i P_{ia}^{Ag \rightarrow CO}(t)$, followed by $P_{e,hc}^{Ag \rightarrow CO} = \sum_a P_a^{Ag \rightarrow CO}(t) \mathcal{G}_a(E)$ (see above) are used to obtain the hot-electron distribution associated with $P_{hc}^{Ag \rightarrow CO}$. The hot-hole distribution $P_{h,hc}^{Ag \rightarrow CO}$ is computed analogously. Using similar arguments, we obtain $P_{hc}^{Ag \rightarrow Ag}$, $P_{hc}^{CO \rightarrow CO}$, and $P_{hc}^{CO \rightarrow Ag}$. The efficiency of a particular partial transition is defined as the ratio of the integral over the partial hot-carrier distribution to the integral of the total hot-carrier distribution.

Fig. 4a shows the direct hot-electron transfer contribution, $P_{hc}^{Ag \rightarrow CO}$, for the three adsorption configurations of CO. The distributions reveal that the direct-transfer process is capable of generating hot electrons with energies up to ~4 eV in the CO molecule. A larger fraction of hot electrons with energies greater than 2 eV can be seen in the case of bridge and hollow configurations, as compared to the on-top configuration. Further, the efficiency of this transition, computed at 27 fs, shows that the direct hot-electron transfer is most efficient when CO is adsorbed in the bridge configuration (1.96%), followed by the hollow (1.78%) and on-top (0.86%) configurations (Fig. 4b). This shows that the direct hot-electron transfer depends on the adsorption configuration of the adsorbate.

Fig. 4c shows the direct hot-hole transfer contribution, $P_{hc}^{CO \rightarrow Ag}$. It is interesting to note that the direct hot-hole transfer contribution is non-zero at the Ag-CO interface. This is because the HOMO level of the CO molecule is expected to lie well below the Fermi level ($E_{HOMO} - E_F > \omega_p$ = 3.74 eV). The efficiency of this transition at 27 fs is found to be 0.16%, 0.52% and 0.49% for the on-top, bridge and hollow positions, respectively (Fig. 4d). These small, but non-zero values are attributed to the transitions arising from the hybridized states (of HOMO and LUMO with the states of the Ag nanoparticle) that are pushed below the Fermi level upon bond formation. This is more evident in the case of the bridge and hollow configurations as peaks in the hot-hole distribution develop near the Fermi level (see Fig. 4c).

Because the Ag nanoparticle is much larger in volume compared to the CO molecule, a major fraction of the hot carriers (~97.5-99% efficiency) are generated via the partial transition $P_{hc}^{Ag \rightarrow Ag}$ (part of the indirect-transfer process). If the number of CO molecules adsorbed on the Ag₁₄₇ nanoparticle is increased or if a smaller Ag nanoparticle is chosen, this fraction is expected to decrease. Further, to check if the choice of the plasmon decay time point (27 fs) has any influence on the results, we computed the efficiency values of the direct-transfer transitions in the immediate time range 27–30 fs (Fig. 4b and c). Our results showed little variation in the efficiency values, showing that the plasmon decay has reached a steady state beyond 27 fs.

Conclusions

In summary, we have employed a RT-TDDFT approach to capture and quantify the directtransfer process at a metal-adsorbate (Ag₁₄₇-CO) interface, a process that is difficult to isolate and assess quantitatively in experiments. For a Gaussian laser pulse tuned to the plasmon frequency and with duration of 10 fs, we observed direct hot-electron transfer from the occupied states of Ag to the unoccupied molecular orbitals of CO with an efficiency of 0.86, 1.96 and 1.78% for CO adsorbed at on-top, bridge and hollow sites, respectively. We also observed direct hot-hole transfer and found this to occur with much smaller efficiencies. Thus, our study not only shows that the direct hot-electron transfer at Ag-CO interfaces is possible, but also reveals that CO molecules adsorbed at the bridge and the hollow sites are more likely to undergo a hotelectron-induced photochemical reaction, given all other steps are similar across the three configurations. Our approach could help understand and enhance direct-transfer transitions, paving way for efficient plasmonic catalysis.

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References

- 1. S. Linic, P. Christopher and D. B. Ingram, Nat. Mater., 2011, 10, 911–921.
- 2. S. Linic, U. Aslam, C. Boerigter and M. Morabito, Nat. Mater., 2015, 14, 567–576.
- 3. M. J. Kale, T. Avanesian and P. Christopher, ACS Catal., 2014, 4, 116–128.
- 4. M. L. Brongersma, N. J. Halas and P. Nordlander, Nat. Nanotechnol., 2015, 10, 25–34.
- 5. X.-C. Ma, Y. Dai, L. Yu and B.-B. Huang, *Light Sci. Appl.*, 2016, 5, e16017.
- 6. U. Aslam, S. Chavez and S. Linic, Nat. Nanotechnol., 2017, 12, 1000–1005.
- 7. P. Christopher, H. Xin and S. Linic, *Nat. Chem.*, 2011, **3**, 467–472.
- 8. K. Wu, J. Chen, J. R. McBride and T. Lian, Science, 2015, 349, 632-635.
- 9. C. Boerigter, R. Campana, M. Morabito and S. Linic, Nat. Commun., 2016, 7, 10545.
- S. Tan, A. Argondizzo, J. Ren, L. Liu, J. Zhao and H. Petek, *Nat. Photonics*, 2017, 11, 806–812.
- 11. L. Yan, F. Wang and S. Meng, ACS Nano, 2016, 10, 5452-5458.
- 12. M. J. Kale and P. Christopher, Science, 2015, 349, 587-588.
- 13. O. A. Douglas-Gallardo, M. Berdakin and C. G. Sánchez, J. Phys. Chem. C, 2016, 120, 24389–24399.
- B. Foerster, A. Joplin, K. Kaefer, S. Celiksoy, S. Link and C. Sönnichsen, ACS Nano, 2017, 11, 2886–2893.
- 15. R. Sundararaman, P. Narang, A. S. Jermyn, W. A. Goddard and H. A. Atwater, *Nat. Commun.*, 2014, **5**, 5788.
- 16. A. M. Brown, R. Sundararaman, P. Narang, W.A. Goddard and H.A. Atwater, ACS Nano, 2016, 10, 957–966.
- 17. J. Ma, Z. Wang and L.-W. Wang, Nat. Commun., 2015, 6, 10107.
- 18. G. Tagliabue, A. S. Jermyn, R. Sundararaman, A. J. Welch, J. S. DuChene, R. Pala, A. R. Davoyan, P. Narang and H. A. Atwater, *Nat. Commun.*, 2018, **9**, 3394.
- 19. U. Aslam, V. G. Rao, S. Chavez and S. Linic, Nat. Catal., 2018, 1, 656-665.
- 20. E. Runge and E. K. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997–1000.
- 21. M. Kuisma, A. Sakko, T. P. Rossi, A. H. Larsen, J. Enkovaara, L. Lehtovaara, and T. T. Rantala, *Phys. Rev. B*, 2015, **91**, 115431.
- 22. T. P. Rossi, M. Kuisma, M. J. Puska, R. M. Nieminen and P. Erhart, J. Chem. Theory Comput., 2017, 13, 4779–4790.
- 23. M. J. Kale, T. Avanesian, H. Xin, J. Yan and P. Christopher, *Nano Lett.*, 2014, **14**, 5405–5412.
- 24. P. Hohenberg and W. Kohn, Phys. Rev., 1964, 136, 864-871.
- 25. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, 140, 1133–1138.
- 26. J. J. Mortensen, L. B. Hansen and K. W. Jacobsen, Phys. Rev. B, 2005, 71, 035109.
- 27. J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi,
- J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm- Møller, M. Strange, G. A. Tritsaris, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, K. S. Thygesen and K. W. Jacobsen, *J. Phys.: Condens. Matter*, 2010, 22, 253202.
- 28. P. E. Blöchl, Phys. Rev. B, 1994, 50, 17953-17979.
- 29. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.

- 30. A. H. Larsen, M. Vanin, J. J. Mortensen, K. S. Thygesen and K. W. Jacobsen, *Phys. Rev. B*, 2009, **80**, 195112.
- 31. T. P. Rossi, S. Lehtola, A. Sakko, M. J. Puska and R. M. Nieminen, J. Chem. Phys., 2015, 142, 094114.
- 32. M. Kuisma, J. Ojanen, J. Enkovaara and T. T. Rantala, Phys. Rev. B, 2010, 82, 115106.
- 33. K. Yabana and G. F. Bertsch, Phys. Rev. B, 1996, 54, 4484-4487.
- 34. T. P. Rossi, P. Erhart and M. Kuisma, unpublished.
- 35. E. Kazuma, J. Jung, H. Ueba, M. Trenary and Y. Kim, Science, 2018, 360, 521-526.

Figures



Fig. 1 Schematic representation of the hot-electron transfer process from the metal to the adsorbate via (a) indirect transfer, and (b) direct transfer. E_F , HOMO and LUMO represent the Fermi level, the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. Full and hollow circles denote the electrons and the holes, respectively. A similar scheme can be drawn for the hot-hole transfer process.



Fig. 2 Structural model of the Ag_{147} -CO on-top configuration used in our calculations. Similar structural models for the Ag_{147} -CO bridge and hollow configurations were used. A close-up of the binding sites (on-top, bridge and hollow) are also shown.



Fig. 3 (a) Photoabsorption spectra of the Ag_{147} -CO (on-top, bridge and hollow), Ag_{147} , and CO systems. (b) The applied pulse and the corresponding dipole-moment response in the time-domain for the Ag_{147} -CO on-top configuration is shown. (c) Induced charge densities at 12 and 27 fs. Positive (purple) and negative (red) isosurfaces are shown using the same isovalues in both the plots. (d) The total hot-electron (solid lines and shaded) and hot-hole (dotted lines and unshaded) distributions for the three Ag_{147} -CO configurations computed at 27 fs.



Fig. 4 (a) The hot-electron (solid lines and shaded) and hot-hole (dotted lines and unshaded) distributions generated in CO and Ag sub-systems, respectively, due to the direct hot-electron transfer process from the metal to the adsorbate. (b) The efficiency of the direct hot-electron transfer process in the time range 27-30 fs. (c and d) same as (a) and (b), but for the direct hot-hole transfer process.

TOC description

An *ab initio* computational approach to capture and quantify direct hot-carrier transfer at metalmolecule interfaces in plasmonic catalysis is presented.