



CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

THz-Pulse-Induced Selective Catalytic CO Oxidation on Ru
Jerry L. LaRue, Tetsuo Katayama, Aaron Lindenberg, Alan S. Fisher, Henrik Öström, Anders Nilsson, and Hirohito Ogasawara

Phys. Rev. Lett. **115**, 036103 — Published 15 July 2015

DOI: [10.1103/PhysRevLett.115.036103](https://doi.org/10.1103/PhysRevLett.115.036103)

THz induced selective catalytic CO oxidation on Ru

Jerry L. LaRue¹, Tetsuo Katayama¹, Aaron Lindenberg^{2,3,4}, Alan S. Fisher⁵, Henrik Öström⁶,
Anders Nilsson^{1,6}, and Hirohito Ogasawara^{1,7*}

¹SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory,
Menlo Park, CA 94025, USA

²Stanford PULSE Institute, SLAC National Accelerator Laboratory,
Menlo Park, CA 94025, USA

³SIMES Institute for Materials and Energy Science, SLAC National Accelerator Laboratory,
Menlo Park, CA 94025, USA

⁴Department of Materials Science and Engineering, Stanford University,
Stanford, California, 94305, USA

⁵Accelerator Directorate, SLAC National Accelerator Laboratory,
Menlo Park, CA 94025, USA

⁶Department of Physics, AlbaNova University Center, Stockholm University,
SE-10691 Stockholm, Sweden

⁷Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory,
Menlo Park, CA 94025, USA

*Correspondence to: hirohito@slac.stanford.edu

We demonstrate the use of intense, quasi-half-cycle THz pulses, with an associated electric field component comparable to intramolecular electric fields, to direct the reaction coordinate of a chemical reaction by stimulating the nuclear motions of the reactants. Using a strong electric field from a THz pulse generated via coherent transition radiation from an ultrashort electron bunch, we present evidence that CO oxidation on Ru(0001) is selectively induced, while not promoting the thermally induced CO desorption process. The reaction is initiated by the motion of the O atoms on the surface driven by the electric field component of the THz pulse, rather than thermal heating of the surface.

PACS numbers: 68.43.-h, 82.53.St, 68.43.Fg, 73.20.Mf

When chemical bonds break or form during catalytic reactions on metal surfaces, the rearrangement of these bonds proceed through the excitations of nuclear motions along the reaction coordinate. The dynamics of these excitations, which include phonons in the substrate as lattice vibrations, and various translational and rotational vibrational motions of adsorbed reactants, occur on 10 femtoseconds to sub-picosecond timescales [1-9]. When these motions are thermally excited, energy is rapidly dissipated into all the nuclear degrees of freedom. The reaction then proceeds down all the potential reaction coordinates, leading to a distribution of final products. Tuning of the geometric and electronic structure of catalytic material can push the chemical reaction towards certain directions. As the reactants and intermediates have opposing dependences on reactivity with respect to bond strength at the active sites, there is a limit to the degree of selectivity [10].

The addition of an external driving force has been explored to enhance the selectivity beyond these limitations of catalytic materials. Strong electric fields above 1 V/nm have been used to induce field desorption of ions, atoms and molecules from surfaces [11, 12], and the field induced processes have been used to initiate and characterize catalytic reactions [13]. Individual atoms and molecules can be manipulated on surfaces using localized electric fields with Scanning Tunneling Microscopy (STM) [14]. More recently, calculations have shown that strong external electric fields perpendicular to the surface and of the same order of magnitude (1 V/nm), as used in this study, have the potential to push or pull an entire layer of water molecules adsorbed on Au by as much as 0.5 Å [15]. It has been suggested that such effects can be enhanced at protrusions in the surface, such as step sites, where the electric fields can be enhanced by as much as a factor of 5 [16]. Other calculations have shown that when an external electric field interacts with a metal surface, the electrons in the conduction bath will migrate towards or away from the surface, depending on the polarization of the electric field [16, 17].

One of the key challenges in chemical reactivity is selectivity, where the desired reaction channel is enhanced in comparison to other competing channels. CO desorption and CO oxidation on the coadsorbed phase of CO and O on Ru(0001) have been extensively studied using thermal excitations and femtosecond optical laser pulses [1, 18-20]. Exposure of O on Ru(0001) to gaseous CO above 400 K

produces CO₂ [20]. However, with thermal excitation under ultra-high vacuum conditions, the coadsorbed phases of CO and O on Ru(0001) is not an active for CO oxidation, in which only CO desorption being stimulated at a temperature of 370 K [21, 22]. When the system is excited through electron-hole pair creation by a femtosecond optical laser pulse, both CO desorption and CO oxidation occur [1]. The hot electrons created by the femtosecond laser pulse transfer energy to the O atoms [6]. The hot electrons eventually cool down, resulting in an electronically ground state O atom with an excess of vibrational energy, i.e. nuclear motion. The excited nuclear motions allow the O atoms to move more freely on the surface, leading to collisions with the CO molecules in the transition states with the subsequent formation of CO₂ [9]. The femtosecond optical laser reaction selectivity for CO oxidation is, however, small at only ~3% compared to CO desorption with near-infrared excitation [1].

In the present study, we utilized quasi-half-cycle, ultrashort, intense THz pulses with an electric field component on the order of 1 V/nm to stimulate the nuclear motions of the adsorbates in order to direct a chemical reaction. We investigated the coadsorbed phase of CO and O on a Ru(0001) surface. We demonstrate that an ultra-short, quasi-half-cycle THz pulse with a strong electric field strength can drive the reaction solely towards CO oxidation to produce CO₂. This is in contrast to femtosecond optical laser excitation, which leads to both CO desorption and CO oxidation with CO desorption being the favored pathway, and heating, which results only in pure CO desorption [1].

We used quasi-half-cycle, broadband THz pulse with peak fields of ~1 V/nm (10 MV/cm) and a peak frequency of 10 THz to induce CO oxidation on the coadsorbed phase of CO and O on Ru(0001) in ultra high vacuum (UHV) at a temperature of 300 K, see the Supplemental Material [23] . At room temperature, a saturated layer of CO and O on Ru(0001), CO/O/Ru(0001), has a 2:1 ratio of 0.5 monolayer coverage (ML) O and 0.25 ML CO, which consists of a mixture of two domains. One domain consists of hollow site O in a honeycomb (2×2) lattice and on-top site CO, the other consists of hollow site O in a p(2×1) lattice and asymmetric on-top site CO [21, 22]. The sample was exposed to an average of 95 pulses of THz radiation at 20° surface grazing angle. The THz pulse generated using coherent transition radiation from ultrashort relativistic electron bunch at the Linac Coherent Light Source (LCLS)

at the SLAC National Accelerator Laboratory [24-26]. The electric field of these THz pulse has both transverse and longitudinal components at the focus due to the radial polarization of the pulse. The applied electric field generates a polarization within the sample which then screens the applied field. The electric field vectors perpendicular to the surface will interact differently with the surface than electric field vectors parallel to the surface. An electric field vector perpendicular to the surface with a peak frequency of 10 THz will decay within the first few tens of nanometers into the substrate [27, 28]. The surface layer will be affected by the presence of the external electric field, with shifts in the electronic densities either towards or away from the surface atoms. This can cause partial ionization of surface metal atoms, or other atoms adsorbed on the surface. In contrast, it is expected that an electric field parallel to the surface will not shift the electron density towards or away from the surface atoms, but will instead induce instantaneous surface currents.

Here we use temperature programmed desorption (TPD) to titrate both coverage and binding site of CO due to THz radiation. First, we evaluated the THz-induced CO desorption reaction on CO/Ru(0001), a surface containing a saturated coverage of pure CO in a $(2\sqrt{3} \times 2\sqrt{3})$ configuration (0.66 ML). Figure 1 shows the TPD traces before and after THz irradiation contain the CO $(2\sqrt{3} \times 2\sqrt{3})$ configuration, indicating that no CO was desorbed.

The reaction yield for CO oxidation was determined by measuring the THz-induced surface coverage loss of CO and O. To determine the surface coverage loss, we quantified the surface coverages of CO and O before and after the THz irradiation using TPD. Figure 2 shows a CO TPD trace before THz irradiation and a series of two CO TPD traces following THz irradiation that were used to determine the CO and O coverages. The CO₂ that is formed from reacting CO and O adsorbates immediately desorbs, as the CO₂ desorption temperature on Ru(0001) is 100 K [29]. In Fig. 2, we compare the CO TPD traces of a saturated CO/O/Ru(0001) surface before THz irradiation (a) and the first CO TPD measurement following THz irradiation (b). From this, we deduce that about a third of the CO is desorbed from the surface. This results in a remaining CO coverage of 0.17 ± 0.01 ML. During THz-induced CO oxidation,

both CO and O are depleted from the surface to produce CO₂. The CO and O removed from the surface open up islands of vacancies, which was confirmed by the desorption profile of readsorbed CO on these vacancies. Following the first CO TPD after THz irradiation, we re-dosed 10 Langmuirs of CO onto the surface at 300 K and recorded another CO TPD to measure the amount of adsorbed O after THz irradiation. The desorption profile of readsorbed CO differs from that of CO/O/Ru(0001), but resembles that of pure CO adsorbed into islands [21]. By comparing the CO TPD trace to the known CO TPD dependence on O coverage, we found that ~16% of the O desorbed from the surface, resulting in a final coverage of 0.42 ± 0.01 ML. Similar amounts of CO and O are removed from the surface following THz irradiation, 0.08 ± 0.01 ML and 0.08 ± 0.01 ML, respectively. That is, that they are removed from the surface with a one-to-one stoichiometric ratio, strongly supporting the conclusion about the formation of CO₂.

This shows that THz irradiation deposits the energy selectively into the O atoms to induce CO oxidation. If the energy was instead deposited into the CO molecules or Ru(0001) substrate, CO desorption would occur. In previous experiments with optical lasers, there was no detectable CO desorption at the rather small absorbed fluence of 2 J/m^2 used in the present experiment [8, 30].

These conclusions are further supported by two-temperature model and empirical friction calculations. We computed the electron, phonon and adsorbate temperatures using the methods and material parameters described in Ref. [8]. We obtained an increase of the phonon temperature by 23 K, whereas for the electron system a temperature jump of 370 K for the Ru(0001) surface after absorption of the THz pulse. The computed temperature of the adsorbate system went up by 70 K to 370 K, which is slightly above the desorption temperature of CO adsorbed onto Ru(0001). Due to the short life-time of the adsorbate excitation [2, 7], the temperature in reactions induced by femtosecond laser pulses typically has to be far above the thermal desorption temperature for a substantial reaction yield[6, 8, 30]. For the present conditions we computed a desorption yield in the range of 10^{-15} ML per THz pulse, which is negligible and will not lead to any detectable CO desorption, in agreement with our experimental result. As it has been shown that the femtosecond temperature-induced reaction yield for CO oxidation is lower

than for CO desorption [1], we can therefore conclude that the THz-induced CO oxidation presented here is not a result of the THz-induced surface temperature rise, but another mechanism is required to explain the observed THz induced CO oxidation.

Since CO oxidation is stimulated, but not CO desorption, the O has to be activated selectively by the THz pulse. In the following we will discuss the plausible mechanism for this selective excitation. The intense electric field of the THz pulse induces a strong polarization in the electronic bath at the surface [16]. For the duration of the THz pulse (<70 fs), the conduction electrons will be both polarized towards the surface, increasing the electron density, and polarized away from the surface, decreasing the electron density, depending on the sign of the electric field vector. When the electron density of the top-most layer is increased due to a polarization towards the surface, the conduction electrons will migrate to previously unoccupied states. On Cu(100), a migrating charge of up to $0.34 e^-$ has been estimated under the exposure to an external electric field of 8 V/nm [16]. In Fig. 3, the electronic structure of the Ru-O and Ru-CO bonds are schematically shown indicating the difference in nature of the states close to the Fermi level. In the case of O on transition metals, the energy position of metal-O antibonding orbital is located near the Fermi level dictates the bond strength [31]. When the electron density is polarized towards the surface, conduction electrons can transfer to the Ru-O antibonding orbital, which will weaken the Ru-O bond, increasing the bond distance [Fig. 4(a)]. This will occur on a timescale on the order of the Ru-O vibration, ~ 50 fs. After interaction with the THz pulse, the electron bath will return to an un-polarized state and the electron will migrate back to the conduction electron bath, leading to vibrationally excited O atoms [Fig. 4(b)]. These excited O atoms will gain additional translational energy on the surface to react with CO to form CO_2 . Whereas the Ru-O bond near the Fermi level has anti-bonding character, the Ru-CO bond has non-bonding character [32, 33] and occupation of these states will have minimal impact on the Ru-CO bond.

One might expect all of the CO molecules to react, but the maximum observed reaction efficiency for CO oxidation suggests that a third of the CO molecules participate in the reaction. As the surface contains mixed domains of CO and O coadsorbed phases, the THz induced reaction would be specific to the local

arrangement of reactants [21, 22]. As it is observed in thermal catalysis, the THz induced reaction could also preferentially occur at the boundary between the two domains [34]. As the O coverage decreases on the surface after THz exposure there will be more stable adsorption sites available for CO [21], making it less likely to react. Additionally the CO and O adsorbates will collide less frequently at lower coverage, which further limits the reaction yield.

We have selectively directed the oxidation of CO on Ru(0001) by using coherent THz radiation from an ultrashort electron bunch. The distinct nature of bond character between Ru-O and Ru-CO allows the strong electric field of THz radiation to activate the Ru-O bond selectively. This mechanism steers the reaction towards the oxidation, whereas the CO desorption dominates in thermal and optical laser stimulated reactions. These results demonstrate the use of strong and ultrashort electric fields to selectively drive reactions at metal surfaces for heterogeneous catalysis.

Acknowledgments

This work is supported by the US Department of Energy, Basic Energy Science through the SUNCAT Center for Interface Science and Catalysis. Portions of this research were carried out at the Linac Coherent Light Source, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University.

References

- [1] M. Bonn, S. Funk, C. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf, and G. Ertl, *Science* **285**, 1042 (1999).
- [2] M. Bonn, C. Hess, S. Funk, J. H. Miners, B. N. J. Persson, M. Wolf, and G. Ertl, *Phys. Rev. Lett.* **84**, 4653 (2000).
- [3] M. Bauer, C. Lei, K. Read, R. Tobey, J. Gland, M. M. Murnane, and H. C. Kapteyn, *Phys. Rev. Lett.* **87**, 025501 (2001).
- [4] Y. Matsumoto, and K. Watanabe, *Chem. Rev.* **106**, 4234 (2006).
- [5] C. Frischkorn, and M. Wolf, *Chem. Rev.* **106**, 4207 (2006).
- [6] M. Dell'Angela *et al.*, *Science* **339**, 1302 (2013).
- [7] M. Beye *et al.*, *Phys. Rev. Lett.* **110**, 186101 (2013).

- [8] J. Gladh, T. Hansson, and H. Öström, *Surf. Sci.* **615**, 65 (2013).
- [9] H. Öström *et al.*, *Science* **347**, 978 (2015).
- [10] L. Grabow, B. Hvolbæk, and J. Nørskov, *Top. Catal.* **53**, 298 (2010).
- [11] Y. Suchorski, W. A. Schmidt, N. Ernst, J. H. Block, and H. J. Kreuzer, *Progress in Surface Science* **48**, 121 (1995).
- [12] Y. Suchorski, N. Ernst, W. A. Schmidt, V. K. Medvedev, H. J. Kreuzer, and R. L. C. Wang, *Progress in Surface Science* **53**, 135 (1996).
- [13] N. Kruse, and T. V. de Bocarmé, in *Handbook of Heterogeneous Catalysis* (Wiley-VCH Verlag GmbH & Co. KGaA, 2008).
- [14] D. M. Eigler, and E. K. Schweizer, *Nature* **344**, 524 (1990).
- [15] A. Huzayyin, J. H. Chang, K. Lian, and F. Dawson, *J. Phys. Chem. C* **118**, 3459 (2014).
- [16] F. Djurabekova, S. Parviainen, A. Pohjonen, and K. Nordlund, *Phys. Rev. E.* **83**, 026704 (2011).
- [17] M. B. Partenskii, V. E. Kuzema, and V. I. Fel'dman, *Soviet Physics Journal* **24**, 985 (1981).
- [18] D. W. Goodman, C. H. F. Peden, and M. S. Chen, *Surf. Sci.* **601**, L124 (2007).
- [19] R. Blume *et al.*, *J. Catal.* **239**, 354 (2006).
- [20] T. E. Madey, H. Albert Engelhardt, and D. Menzel, *Surf. Sci.* **48**, 304 (1975).
- [21] K. L. Kostov, H. Rauscher, and D. Menzel, *Surf. Sci.* **278**, 62 (1992).
- [22] F. M. Hoffmann, M. D. Weisel, and C. H. F. Peden, *Surf. Sci.* **253**, 59 (1991).
- [23] See Supplemental Material for details of (a) experimental setup (b) sample preparation (c) coverage estimation.
- [24] A. S. Fisher, *Synchrotron Radiation News* **26**, 30 (2013).
- [25] Z. Wu, A. S. Fisher, J. Goodfellow, M. Fuchs, D. Daranciang, M. Hogan, H. Loos, and A. Lindenberg, *Rev. Sci. Inst.* **84**, 022701 (2013).
- [26] D. Daranciang, J. Goodfellow, M. Fuchs, H. Wen, S. Ghimire, D. A. Reis, H. Loos, A. S. Fisher, and A. M. Lindenberg, *Appl. Phys. Lett.* **99**, 141117 (2011).
- [27] Using the complex part of the refractive index of ruthenium, $n = 23 + i110$ extrapolation of known value to 10 THz, penetration depth of 21 nm of the absorbed energy was determined. Consequently the electric field has a penetration depth of 42 nm.
- [28] E. D. Palik, *Handbook of Optical Constants of Solids* (Academic Press, San Diego, 1998).
- [29] F. M. Hoffmann, M. D. Weisel, and J. Paul, *Surf. Sci.* **316**, 277 (1994).
- [30] S. Funk, M. Bonn, D. N. Denzler, C. Hess, M. Wolf, and G. Ertl, *J. Chem. Phys.* **112**, 9888 (2000).
- [31] T. Anniyev, S. Kaya, S. Rajasekaran, H. Ogasawara, D. Nordlund, and A. Nilsson, *Angew. Chemie* **124**, 7844 (2012).
- [32] A. Föhlisch, W. Wurth, M. Stichler, C. Keller, and A. Nilsson, *J. Chem. Phys.* **121**, 4848 (2004).
- [33] A. Nilsson, and L. G. M. Pettersson, *Surf. Sci. Rep.* **55**, 49 (2004).
- [34] T. Engel, and G. Ertl, in *Advances in Catalysis*, edited by H. P. D.D. Eley, and B. W. Paul (Academic Press, 1979), pp. 1.

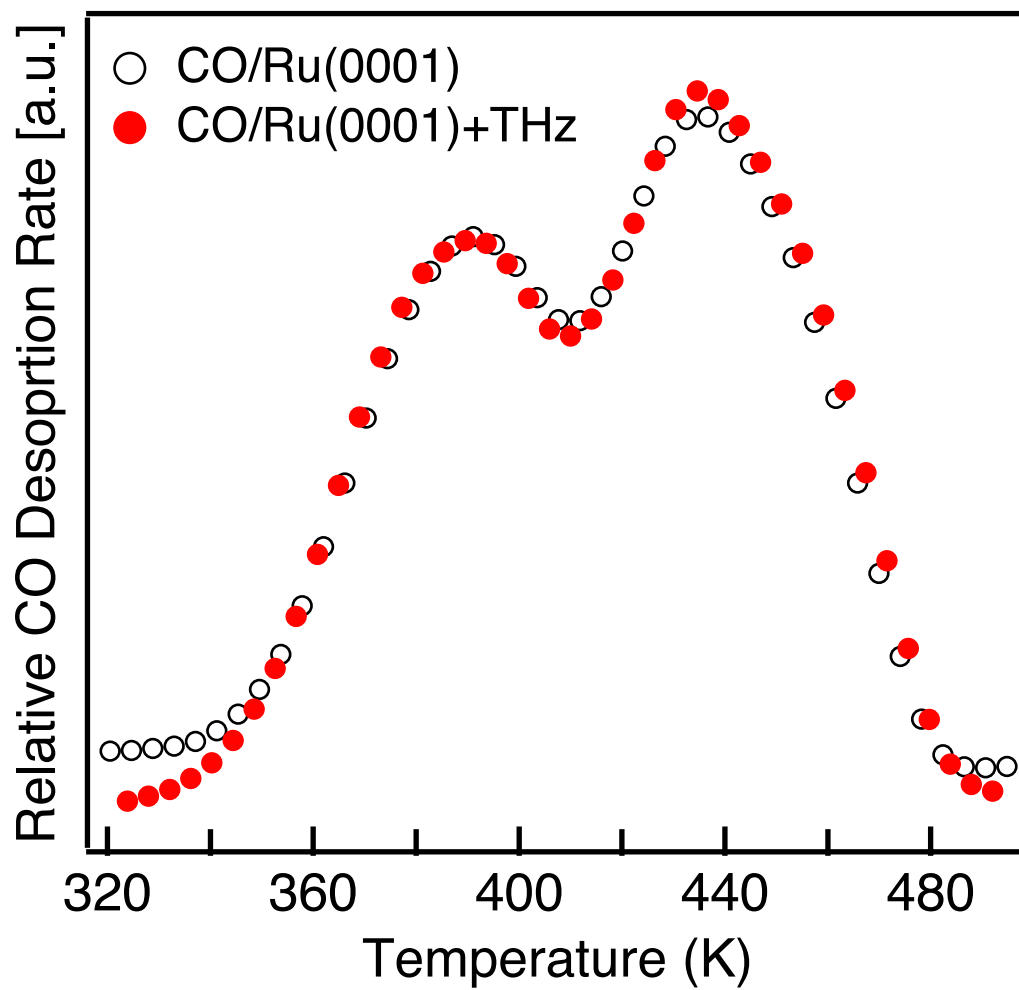
Figure Captions

FIG. 1. CO temperature programmed desorption (TPD) traces of CO/Ru(0001) before and after THz radiation. No CO desorption was induced by THz radiation.

FIG. 2. CO temperature programmed desorption (TPD) traces of CO/O/Ru(0001): (a) before THz irradiation; (b) after THz irradiation; (c) after THz irradiation and re-dosed with a CO to form a saturated CO layer. The ratio between (a) and (b) measures the decrease in CO coverage after THz irradiation. In (c), the desorption peak for re-dosed CO appears at high-temperature side, 380 – 430 K, which is assigned to the desorption of CO from O depleted regions. No CO desorption was found above 450 K.

FIG. 3. Schematic of the molecular orbitals of O and CO bonding to the Ru surface. The anti-bonding Ru-O orbitals and the Ru-CO non-bonding orbital are crossing the Fermi level. These orbitals will be further populated as conduction electrons are polarized towards the surface. The Ru-O bond will be weakened due to the partial filling of the anti-bonding orbital while the Ru-CO bond will be unaffected due to the non-bonding character of the orbital.

FIG. 4. Strong electric field stimulated surface chemistry. In the presence of the THz field, (a) Conduction electrons are polarized towards the surface due to the intense electric field and an electron occupation of the Ru-O antibonding orbital elongates the Ru-O bond. In the absence of the THz field, (b) the electron transfers back to the surface leaving vibrationally excited the Ru-O bond leading to CO oxidation to produce CO₂.



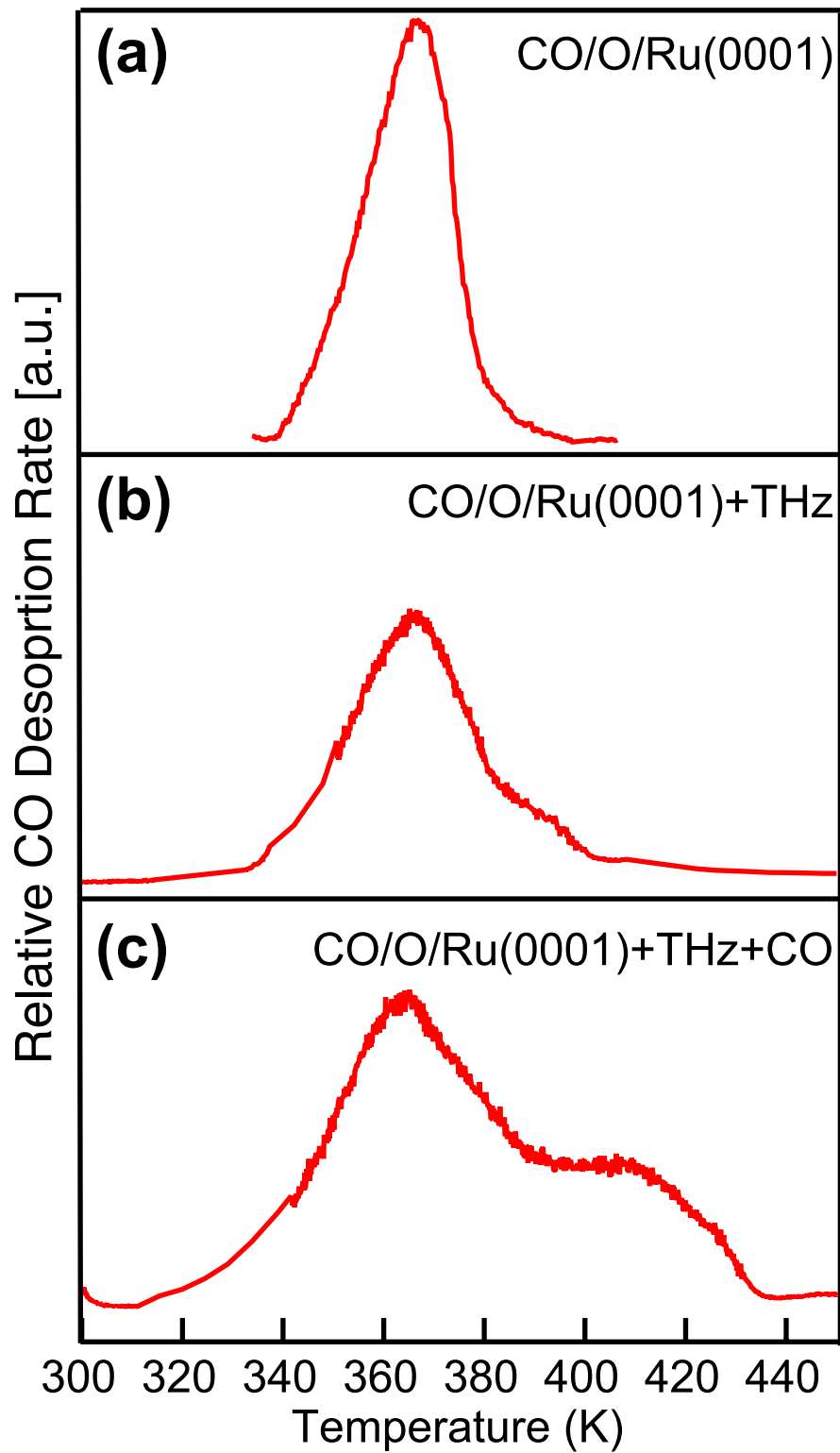


Figure 2

LC15247

13APR2015

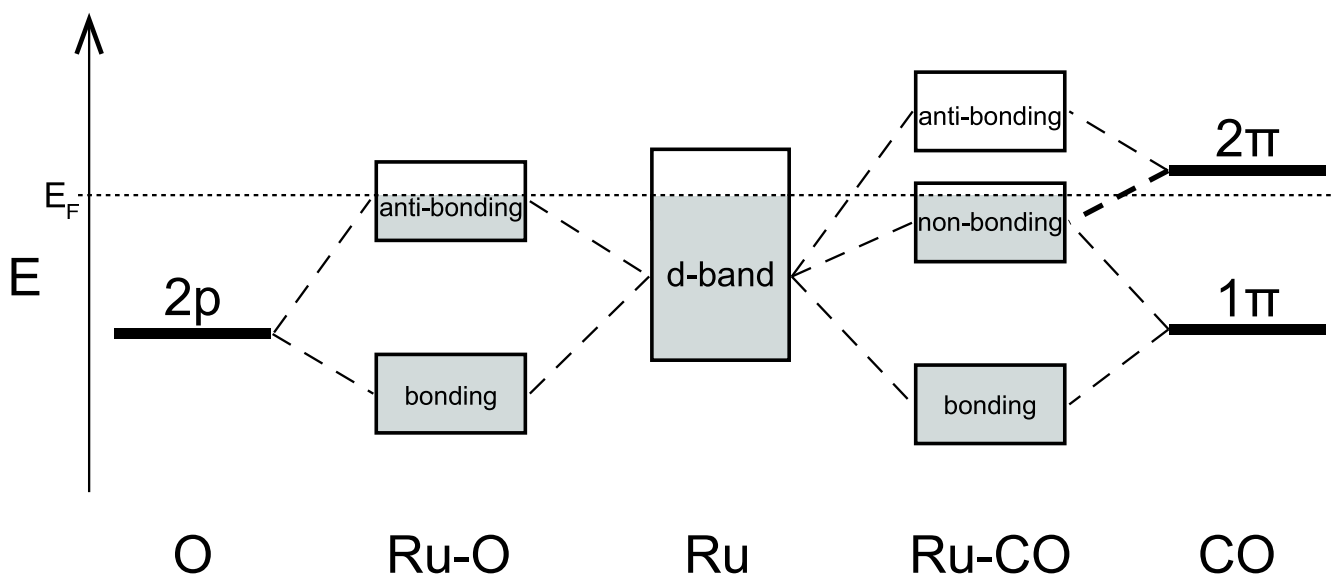
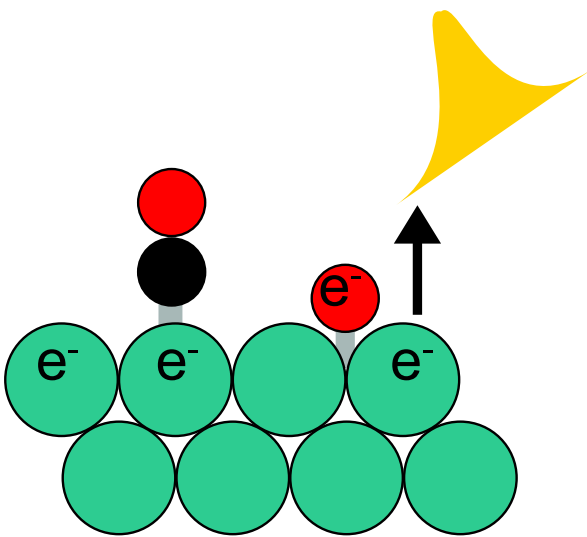


Figure 3

LC15247

13APR2015

(a)



(b)

