



In situ manipulation of the d-band center in metals for catalytic activity in CO oxidation†

 Kyung Rok Lee,^{‡,a} Danim Yun,^{‡,a} Dae Sung Park,^b Yang Sik Yun,^a
Chyan Kyung Song,^a Younhwa Kim,^a Jungwon Park^a and Jongheop Yi^{*,a}

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A combination of *in situ* XANES, temperature programmed oxidation, kinetic and density functional theory results demonstrate that the d-band centers (ϵ_d) of Au and Pt metals are upshifted when 39.9 V m⁻¹ of electric field is applied. This leads to the enhancement of the adsorption strength of CO on both metals, and, thus, results in the promotion (+15%) and the depression (–23%) of CO conversions on Au and Pt, respectively, in the CO oxidation.

Selective bond breakage and formation are essential to obtaining the desired products in heterogeneous catalysis. Chemical bond activation depends on the adsorption behavior between a reactant (or a product) and a catalytic active site, which is influenced by the electronic structure of either the adsorbate or the adsorbent.^{1–4} Therefore, the fundamental understanding of the electronic structure that results from adsorbate–surface interaction is a significant determinant of which catalyst could selectively produce the target materials. The d-band center (ϵ_d) is now considered one of the reactivity descriptors in the theoretical background of d-band models that are used to estimate surface chemisorption.^{5–8} In this model, the catalytic active site with the higher ϵ_d generally shows the stronger adsorption with adsorbates, because the empty antibonding states are created.^{1,7–9}

Based on this theoretical background, the d-band theory has been applied in experimental investigations to enhance the catalytic performance.^{4,10–14} V. R. Stamenkovic *et al.* observed that Pt₃Ni is less vulnerable to the poisoning of the active site during the oxygen reduction reaction (ORR) than a Pt catalyst due to a downshift of ϵ_d at the bimetallic surface.⁴ H. Abe *et al.* also demonstrated that a downshift in the ϵ_d of Pt₃Ta leads to the weakening of the adsorption strength of CO.¹⁰ In addition,

N. Acerbi and E. Tsang reported that the ϵ_d of the active metal was an effective descriptor to elucidate the inverse volcano trend of the activation energy for H₂ dissociation.¹¹ Y. Sun *et al.* showed that the ϵ_d of Pt is decreased by N-doped graphene and that the stability of Pt was improved by the weak desorption of CO, which is regarded as an inhibitor of methanol oxidation.¹²

To reveal the relationship between the ϵ_d and catalytic performance, previous studies have depended on designing supported materials such as doped metal oxides^{12,13} or adding other elements.^{4,10,14} These methods focused on synthesis are quite complicated, and it would be insufficient to validate the influence of ϵ_d on catalysis alone due to the other varied catalytic properties. These limitations suggest the necessity for further study to demonstrate the effect of ϵ_d on catalysis.

Here, we used a novel catalytic system to directly control the ϵ_d of an active metal and experimentally confirmed the relationship between the ϵ_d and catalytic activity. With our system, an electric field was formed through a supported metal catalyst connected in a closed circuit, which led to a modification of the d-band structure. The controlled electronic structures in active metal nanoparticles, Pt and Au, were observed by *in situ* X-ray absorption near edge structure (XANES) analysis. The effect that the adsorption behavior of CO exerted on catalytic performance with and without current-flow was examined by *in situ* temperature programmed oxidation (TPO) and kinetic studies. Density functional theory calculations were conducted to describe the adsorption behavior of a gas molecule in the electric field. Our reaction system exhibited that catalytic behavior during CO oxidation is able to be manipulated and it depends on the state of the ϵ_d . Based on these results, we concluded that appropriate modification of the electronic structure changes the adsorption energy of reactants, which leads to high activity for the target reaction.

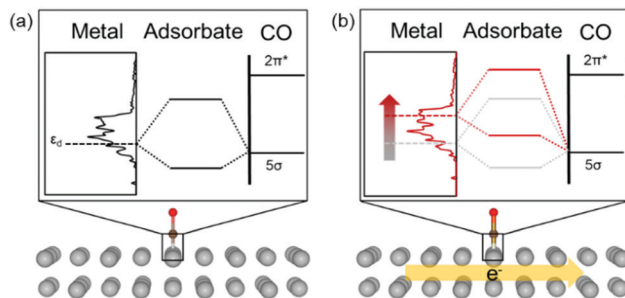
According to the Blyholder and d-band models,^{15,16} the energy states of bonding and antibonding orbitals depend on the ϵ_d of the metal surface, which is explained in Scheme 1(a). When the ϵ_d of a metal shifts upward, the antibonding orbital is located at the higher state.^{9,17,18} The vacancy in the

^a School of Chemical and Biological Engineering, Seoul National University, 1, Gwanak-ro, Gwanak-gu, Seoul, Republic of Korea. E-mail: jyi@snu.ac.kr

^b Center for Convergent Chemical Process, Korea Research Institute of Chemical Technology, Daejeon, 34114, Republic of Korea

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‡ These authors contributed equally to this work.



Scheme 1 Schematic explanation for reaction system and band structure (a) without and (b) with electric current. Grey, brown and red spheres represent metal, carbon and oxygen atoms, respectively.

antibonding state is then increased compared to that in the conventional catalysis, which enhances the bonding strength. When either the metal or semiconductor is placed between the electric field, the electronic band and the shape of the density of state of those materials are modified due to the applied potential.^{19,20} Consequently, this allows a chance to manipulate the ϵ_d of the supported metal catalyst when connected to a closed circuit as shown in Scheme 1(b). Platinum and gold have unfilled and filled d states and are expected to exhibit different catalytic activities for CO conversion.^{7,21} Due to this difference of d state in both metals and the environmental and industrial significances of CO oxidation, CO oxidation over Pt and Au catalysts was used as a model reaction. It was expected that increase of the ϵ_d induced by applied potential would lead to a stronger adsorption of CO but different effects on turnover rates for CO oxidation over the Pt and Au catalysts.

Our previously reported catalytic system, a current-assisted catalytic system,²² was used to prove this concept and described in Fig. S1 (ESI[†]). The difference is the range of applied voltage during catalysis to focus on the electronic effect excluding the Joule heating. The increase of temperature as a function of applied voltage was confirmed by experiments and COMSOL calculations. Fig. S2 and S3 (ESI[†]) show that the increase of temperature by applying 0.4 V is lower than 2 °C. This suggests only 0.6–1.3% increases because of Joule heating and this effect is negligible. Based on these results, the range of applied

voltage in this study was planned as less than 0.4 V, which means that the magnitude of the electric field at the catalytic bed is 39.9 V m⁻¹ (Section S1.3 and Table S2, ESI[†]).

To minimize the size effect of metals on catalysis, we synthesized both catalysts with similar and uniform metal size. The Au and Pt nanoparticles were 10.9 ± 2 and 10.2 ± 1.5 nm in size, respectively. Other morphological properties of the prepared catalyst were characterized by TEM, XRD and BET analysis (Fig. S4 and S5, ESI[†]).

In order to confirm the changes in ϵ_d , the electronic structure of Pt and Au during increase in the voltage applied to the catalytic system were evaluated by *in situ* X-ray absorption spectroscopy (*in situ* XAS, Fig. 1(a) and (b)). The white line in Fig. 1(a) marks a sharp and narrow absorption peak at 11 567 eV, which means that the Pt on the carbon support maintained its metallic state²³ in the electric field for all samples. Interestingly, an increase in the white line was confirmed with increasing external potential from 0.0 V to 0.8 V. This observation represents that the unoccupied 5d_{3/2} and 5d_{5/2} states of Pt were expanded to higher state^{6,23,24} due to the external electrical energy and it reveals an up-shift in the ϵ_d . The white line intensity is initially inclined sharply but became nearly constant with increasing the applied voltage. This indicates that electron transition from lower to upper states sharply increased when the voltage was relatively low (≤ 0.4 V), and gradually became saturated at high voltage (> 0.4 V). On the Au catalyst, the same behavior of increased Au L₃ edge was exhibited at 11 920 eV in Fig. 1(b). It was concluded that the ϵ_d increases until the value is saturated as a function of applied voltage. Also, when the applied electric field is 0.4 V, the effect of modified ϵ_d is maximized and the thermal issue is negligible.

Since the adsorption of gas molecules on the metallic surface is influenced by the interaction between the molecular orbital and the band structure of the metal, the adsorption strengths of CO onto the Pt surface without and with applied voltage were verified by CO-temperature-programmed oxidation (TPO). For CO-TPO-MS, the CO₂ signal was monitored by mass spectroscopy in oxygen flow with increasing temperature after pre-adsorbing CO. Fig. 1(c) shows the intensities of the CO₂ signal of Pt/C when the applied voltage was 0 and 0.4 V. For a conventional reaction system (0 V), the Pt sample showed one

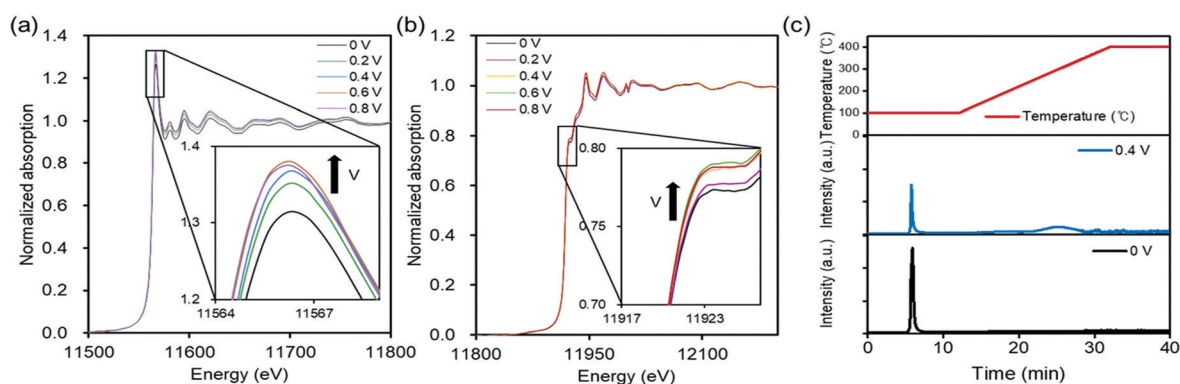


Fig. 1 *In situ* XANES spectra of the (a) Pt and (b) Au L₃ edges according to the various applied voltages. (c) Adsorption behavior of CO on Pt/C with and without applied voltage. CO₂ signal was monitored by *in situ* TPO-MS after pre-adsorbing CO on Pt/C.

peak at 5 minutes. Interestingly, when 0.4 V was applied to the catalytic bed, the intensity of the initial peak decreased and another peak appeared 20–30 minute later. The appearance of the new peak at high temperature represents an enhancement of CO adsorption onto Pt/C, which was caused by the electric field. In the case of Au metal, CO is hardly adsorbed on the metal surface²⁵ at room temperature and it was hard to observe it by CO-TPO-MS as shown in Fig. S6 (ESI[†]).

A catalytic reaction test for CO oxidation on Pt and Au was conducted with and without an electric field. Fig. 2(a) illustrates that CO was more easily converted on Pt than on Au in the conventional reaction system. Interestingly, the conversion rates on each metal exhibited the opposite trend with applied voltage up to 0.4 V (Fig. 2(b)). The Pt/C catalyst showed a negative tendency for CO conversion as the applied potential increases. At 0.4 V, the conversion of CO on the Pt decreased to 23% because the adsorption of CO was too strong on the Pt, which is explained in Fig. 1(c). On the other hand, the electric field positively affected CO conversion on the Au catalyst. According to Fig. 1(b), the electric field moved the ϵ_d of Au above the natural state. This assisted the adsorption of CO, and the conversion rate of CO was promoted as the applied voltage was increased. No sintering or coking of the used catalysts was detected in either of the samples (Fig. S7 and S8, ESI[†]). This means that the applied voltage (~ 0.4 V) does not cause any thermal issue due to Joule heating. Also, we confirmed that the catalytic performances return to the initial levels after applying out electric potential (Fig. S9, ESI[†]); this indicates that irreversible change of the catalyst (*e.g.* facet, defects) does not effect the catalytic performance during applying a voltage.

To investigate the effect of the manipulated ϵ_d on the catalysis mechanism, a kinetic study for CO oxidation on the Pt and Au was performed with and without the electric field. In Fig. 3(a), Pt/C showed two kinds of reaction order for the partial pressure of CO (P_{CO}). When the P_{CO} was in the low range, the reaction order was negative, however, it became nearly zero at the high range of the P_{CO} . According to the previous study, CO adsorbs on the Pt group metal more competitively than O_2 ²⁶ and inhibits the adsorption of O_2 . Due to the finite number of the active site, desorption of CO becomes a rate determining step (RDS) for CO oxidation²⁷ and schematic illustration is exhibited in Fig. S10 (ESI[†]). Lower coverage of CO on the Pt

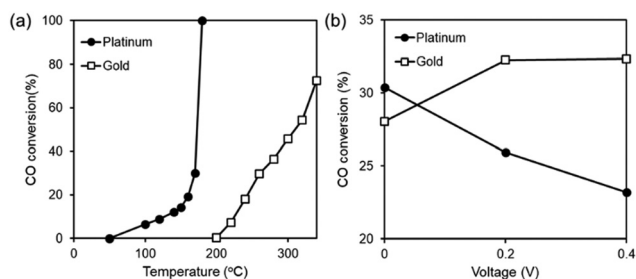


Fig. 2 Catalytic activity of CO oxidation on Pt/C and Au/C with (a) thermal and (b) electric field conditions at 170 °C on Pt/C and 300 °C on Au/C, respectively.

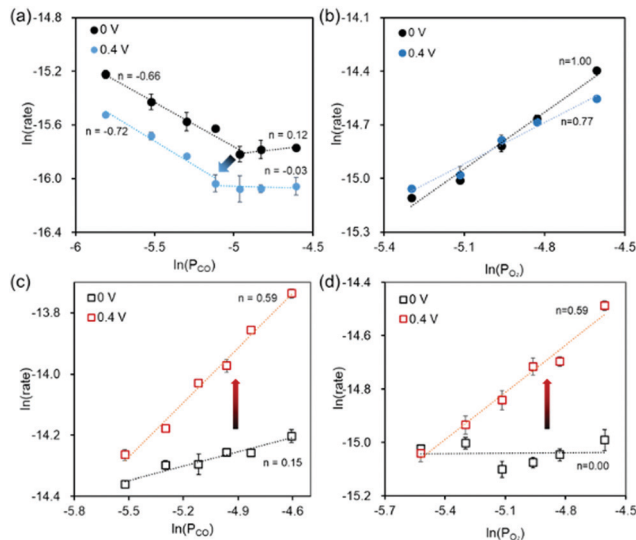


Fig. 3 Kinetic study of CO oxidation for partial pressure of (a) CO and (b) O_2 on the Pt/C and for partial pressure of (c) CO and (d) O_2 on the Au/C with and without applied voltage.

surface is more favorable to conversion of the reactant, which agrees with the profile in Fig. 3(a). As the coverage of CO increases, the reaction rate will be constant due to the limited number of the active sites caused by equilibrium of the adsorption/desorption of CO, which can be observed in a high range of the P_{CO} . When the Pt/C was placed in the electric field, presented as blue dots in Fig. 3(a), the P_{CO} for constant reaction rate was exhibited at lower value than the P_{CO} of the thermal reaction system. Since the nearly zero order in the P_{CO} is originated from the stronger adsorption of CO, the zero-order at lower P_{CO} in the electric field than the conventional system means the enhanced adsorption strength of CO induced by the electric field. The reaction for the partial pressure of O_2 (P_{O_2}) has a first-order rate constant in the thermal system, and was slightly decreased by the electric condition (Fig. 3(b)). This means that the effect of O_2 adsorption on the Pt/C was negligible during the CO oxidation.

A kinetic study of Au/C with electric field was exhibited in Fig. 3(c) and (d). The reaction order for P_{CO} and P_{O_2} on the Au/C with the thermal system was zero, and it increased to 0.59 when the electric field was applied. According to the previous research,²⁸ the interface between an Au nanoparticle and a non-reducible support material, such as carbon, does not participate in the adsorption of gas molecules. The adsorption of CO onto an Au surface is more favorable than that of O_2 , and the activation of O_2 on the Au is assisted by the adsorbed CO during the CO oxidation. Increased reaction order for P_{CO} in the electric field means enhanced adsorption of CO on the Au/C. Reinforced adsorption of CO supported O_2 activation and this phenomenon represented an increased reaction order for P_{O_2} with applied potential, which was elucidated in Fig. S11 (ESI[†]).

Theoretical investigation was conducted by using DFT calculations to support these results acquired from experimental

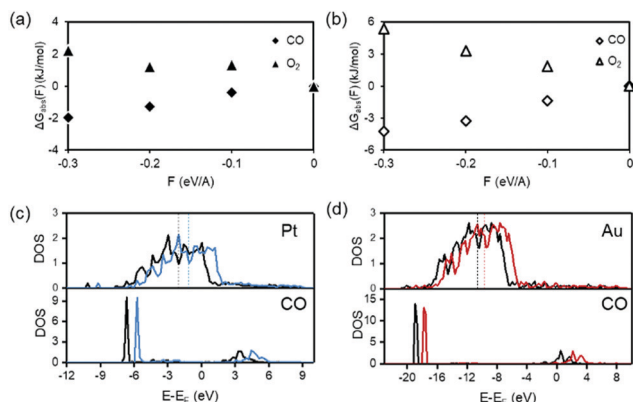


Fig. 4 Difference of adsorption energy for CO and O₂ on (a) the Pt and (b) the Au metal between the electric field and zero field conditions. Density of states of adsorbed CO on (c) the Pt and (d) Au slab: black line represents calculation at 0 eV Å⁻¹, blue and red lines describe calculations at -0.3 eV Å⁻¹, and dashed lines indicate d-band center of each metal, respectively.

studies. We calculated the adsorption energy, a density of state (DOS) and the ε_{d} of the gas-adsorbed metal with and without an electric field. The calculated adsorption energy of gas molecules on each metal surface is presented in Fig. 4(a), (b) and Fig. S12 (ESI[†]), and adsorption of CO and O₂ showed different trends as the electric field increased. The adsorption energy of CO on the Pt and Au at 0.3 eV Å⁻¹ was decreased to 2 and 4 kJ mol⁻¹ compared to the energy without an electric field. However, the adsorption of O₂ on the Pt and the Au surface was weakened with increased electric field. This calculated adsorption behavior of CO and O₂ on each metal is consistent with the results from the kinetic studies in Fig. 3. DOS for the CO and Pt in the electric field was also calculated to identify the origin of the varied adsorption of CO on the Pt and the Au. In Fig. 4(c) and (d), the DOS of the CO π bond was shifted to the higher state due to the lifted ε_{d} of Pt in the z -direction electric field, which explains the increased adsorption energy of CO.

In summary, the catalytic activity of Au and Pt catalysts used in CO oxidation was controlled by modifying the ε_{d} of the metals. The *in situ* XANES results revealed that an electric field manipulated the d-band structure of the metal. This modification enhanced the adsorption strength of CO and varied the catalytic activity of CO oxidation. In the case of Pt, the conversion rate of CO was decreased to 23% due to an excessive adsorption of CO, whereas the activity on Au increased to 15% with the assistance of the applied electric field. This result implies the significance of appropriate d-band structure of the metals to accomplish a target reaction.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- Y. Xu, A. V. Ruban and M. Mavrikakis, *J. Am. Chem. Soc.*, 2004, **126**, 4717–4725.
- V. R. Stamenkovic, B. S. Mun, K. J. Mayrhofer, P. N. Ross and N. M. Markovic, *J. Am. Chem. Soc.*, 2006, **128**, 8813–8819.
- J. Greeley and M. Mavrikakis, *Nat. Mater.*, 2004, **3**, 810–815.
- V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas and N. M. Markovic, *Science*, 2007, **315**, 493–497.
- M. D. Porosoff and J. G. Chen, *J. Catal.*, 2013, **301**, 30–37.
- S. J. Yoo, S. J. Hwang, J.-G. Lee, S.-C. Lee, T.-H. Lim, Y.-E. Sung, A. Wiecekowsky and S.-K. Kim, *Energy Environ. Sci.*, 2012, **5**, 7521–7525.
- B. Hammer and J. K. Nørskov, *Nature*, 1995, **376**, 238–240.
- J. K. Nørskov, F. Abild-Pedersen, F. Studt and T. Bligaard, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 937–943.
- S. Bhattacharjee, U. V. Waghmare and S. C. Lee, *Sci. Rep.*, 2016, **6**, 35916.
- H. Abe, H. Yoshikawa, N. Umezawa, Y. Xu, G. Saravanan, G. V. Ramesh, T. Tanabe, R. Kodiyath, S. Ueda, N. Sekido, Y. Yamabe-Mitarai, M. Shimoda, T. Ohno, F. Matsumoto and T. Komatsu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 4879–4887.
- N. Acerbi, S. C. Tsang, G. Jones, S. Golunski and P. Collier, *Angew. Chem., Int. Ed.*, 2013, **52**, 7737–7741.
- Y. Sun, C. Du, G. Han, Y. Qu, L. Du, Y. Wang, G. Chen, Y. Gao and G. Yin, *Electrochim. Acta*, 2016, **212**, 313–321.
- D. Higgins, M. A. Hoque, M. H. Seo, R. Wang, F. Hassan, J.-Y. Choi, M. Pritzker, A. Yu, J. Zhang and Z. Chen, *Adv. Funct. Mater.*, 2014, **24**, 4325–4336.
- M. McEntee, A. Stevanovic, W. Tang, M. Neurock and J. T. Yates, Jr., *J. Am. Chem. Soc.*, 2015, **137**, 1972–1982.
- G. Blyholder, *J. Phys. Chem.*, 1964, **68**, 2772–2777.
- Y. Morikawa, J. J. Mortensen, B. Hammer and J. K. Nørskov, *Surf. Sci.*, 1997, **386**, 67–72.
- Y. Jiao, Y. Zheng, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, **44**, 2060–2086.
- H. Xin, A. Holewinski, N. Schweitzer, E. Nikolla and S. Linic, *Top. Catal.*, 2012, **55**, 376–390.
- J. O’Keeffe, C. Wei and K. Cho, *Appl. Phys. Lett.*, 2002, **80**, 676–678.
- R. Balu, X. Zhong, R. Pandey and S. P. Karna, *Appl. Phys. Lett.*, 2012, **100**, 052154.
- L. B. Ortiz-Soto, O. S. Alexeev and M. D. Amiridis, *Langmuir*, 2006, **22**, 3112–3117.
- D. Yun, D. S. Park, K. R. Lee, Y. S. Yun, T. Y. Kim, H. Park, H. Lee and J. Yi, *ChemSusChem*, 2017, **10**, 3671–3678.
- S. Mukerjee and R. C. Urian, *Electrochim. Acta*, 2002, **47**, 3219–3231.
- L. Bai, X. Wang, Q. Chen, Y. Ye, H. Zheng, J. Guo, Y. Yin and C. Gao, *Angew. Chem., Int. Ed.*, 2016, **55**, 15656–15661.
- C. Lemire, R. Meyer, S. Shaikhutdinov and H. J. Freund, *Angew. Chem., Int. Ed.*, 2004, **43**, 118–121.
- S. M. McClure and D. W. Goodman, *Chem. Phys. Lett.*, 2009, **469**, 1–13.
- T. A. Matsushima, D. B. Foyt, D. C. Close and J. S. White, *J. Catal.*, 1975, **39**, 277–285.
- M. M. Schubert, S. Hackenberg, A. C. van Veen, M. Muhler, V. Plzak and R. J. Behm, *J. Catal.*, 2001, **197**, 113–122.