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Article

Adsorbed CO induced change of the adsorption site and charge of Au adatoms on FeO(111)/Ru(0001)

Runhai Ouyang, Wei-Xue Li*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

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ABSTRACT

A first principles study of the influence of CO adsorption on the charge state, adsorption site, and stability of Au adatoms on FeO/Ru(0001) was presented. Calculations were first carried out to explore the detailed interface structure of a bilayer FeO(111) film on Ru(0001). The HCP domain inside the Moire supercell has a rather small rumpling with both the Fe and O atoms directly bonded to the Ru substrate. The most stable adsorption of an Au atom on FeO/Ru(0001) is at the Fe-bridge site in the HCP domain, where Au binds with two flipped Fe atoms and is negatively charged. After exposure to CO, the Au anions at the Fe-bridge site changed their position to the O-top site by overcoming a small barrier of only 0.12 eV, where they formed stable Au⁻-CO species with a significant reduction in the formation energy. The results highlighted the importance of in situ characterization of supported catalysts under reaction conditions, and implications on catalyst stability were also discussed.

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1. Introduction

Unlike a bulk oxide polar surface, which is intrinsically unstable, stoichiometric and clean ultrathin oxide polar films can be grown on a metal substrate, which provides an ideal template for the investigation of the influence of polarity on the catalytic properties of a supported catalyst [1–4]. In addition, ultrathin oxide films have their own novel properties that are different from those of the bulk counterpart, such as film structural flexibility, interface coincidence structure between the oxide film and the underlying metal substrate, and permeability of the thin film to electrons [5–7]. These composite systems become more attractive when we are aware of their tunable physical and chemical properties that can be obtained by controlling the oxide film-metal substrate combination and the film thickness. They can be used for the exploration of catalytic structure-activity relationships and the optimization of cata-

lysts [8].

The growth of high quality FeO(111) [9–14], MgO(111) [15,16], CoO(111) [17], and ZnO(0001) [18,19] polar films on a metal substrate have been reported in the literature. In particular, the bilayer FeO(111) film can be grown on Pt [9–12], Ru [14], and Au [13], and all the FeO-metal interfaces have periodic Moire supercells due to the lattice coincidence between the film and the metal substrate. The adsorption properties of a metal atom, clusters, particles, and organic molecules have been well explored on the FeO(111)/Pt(111) support by experiment [20–29] and theory [20,30–34]. It was found that the Moire supercell of FeO(111)/Pt(111) has three domains with different geometric structures and surface dipole moments, which result in domain-preferred adsorption and thus the self-assembly of metal atoms, molecules, and particles on the FeO(111) surface [24,27,29]. Furthermore, the adsorption of metal atoms of high electronegativity can reverse the Fe-O

* Corresponding author. Tel: +86-411-84379996; Fax: +86-411-84374447; E-mail: wxli@dicp.ac.cn

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stacking in the vertical direction of the FeO surface [30,31]. Depending on the domain, the charge of the metal adatoms can be either positive or negative [30]. As compared to the well-studied FeO(111)/Pt(111) system, however, the FeO(111)/Ru(0001) and FeO(111)/Au(111) systems are less studied.

For supported metal catalysts, the charge state, coordination, size, and also the metal-support interface are important for their catalytic performance, and much effort has been dedicated to establish structure-activity relationships [35–41]. The challenge is that the structure and catalytically active sites of the supported catalysts under a reaction environment may be rather different from that existing under ultra high vacuum (UHV) conditions, and this requires in situ characterization. Reactant/reaction induced catalyst sintering, disruption, refaceting, and many other structural changes have been observed in numerous experiments [23,42–49]. Insights on how the reactant affects the geometric and electronic properties of the metal catalyst are of great significance for the understanding of catalytic mechanisms, and the design of stable and active catalyst.

In particular, the interactions between reactants and metal adatoms have a large effect on catalyst stability and activity. For reactant-promoted Ostwald ripening and disintegration of metal particles, it was found that the formation and diffusion of the monomer (basic unit constituting the metal particle) play an important role [45,50–52]. When reactants have a strong interaction with the metal atoms, metal-reactant complexes can form as new monomers, as opposed to the metal atoms, because of their lower formation energy and higher concentration. The metal-reactant complexes may have rather different diffusivities on the supports. For Pt adatoms on the Pt(110) surface, scanning tunneling microscope (STM) images showed that the H atom can adsorb on Pt adatoms to form a H-Pt complex, which has a higher mobility [53]. The interplay between the reactant and metal atom and also the support thus influence metal particle stability greatly, such as promoted sintering and disintegration of metallic Au [23,54], Rh [43,55], and Pt [47,56] under CO and O₂ conditions. Furthermore, the reactant can affect the chemical nature of the supported metal catalyst dramatically. For a MgO-supported Au adatom, the adsorption of CO induced a dramatic charge transfer from the MgO support to the Au adatom, which resulted in a red shift of the CO stretching frequency [57].

In this work, we present a density functional theory (DFT) study on the adsorption of Au atoms on a bilayer FeO(111) polar film on a Ru(0001) substrate, and their response to the adsorption of CO using the Moire superstructure that has been identified by experiment [14]. Unlike the FeO/Pt(111), which is one of the most thoroughly studied model systems, the FeO/Ru(0001) system has not been well studied. Since Ru has a very different lattice constant and reactivity from Pt [14], the investigation of the detailed superstructure and corresponding chemistry of the FeO/Ru(0001) system can provide a new avenue for exploring the surface catalysis of a supported ultrathin oxide film. The exploration of Au adatoms can contribute to the design and optimization of Au catalysts, which have promising applications in energy and environment catalysis [37,58,59].

Finally, we address the effect of the environment using the presence of CO. As shown below, the introduction of CO has a dramatic effect on the adsorption site, charge, and stability of the Au adatoms on FeO/Ru(0001), which could have profound implications in heterogeneous catalysis.

2. Calculation method

First principles spin-polarized DFT calculations were performed using the Vienna ab initio simulation package (VASP) [60], in which the core electron and exchange-correlation interactions were described by projector augmented waves (PAW) [61] and the generalized-gradient approximation in the form of PW91 [62]. The DFT+U approach developed by Dudarev et al. [63] with $U = 4$ and $J = 1$ [30,64] was applied for the proper description of the iron oxide. The FeO/Ru(0001) surface was simulated using the measured Moire superstructure (7×7)R0°-FeO(111)/(8×8)-Ru(0001) [14], in which the O-Fe bilayer was supported on three layers of Ru slabs. The initial magnetic structures of the FeO bilayer were set to be anti-ferromagnetic. The wave function was expanded by plane waves with a kinetic cut-off of 350 eV. The change in the calculated adsorption energy using a higher cut-off of 400 eV was less than 5 meV. The charges of the adatoms were obtained using the Bader scheme [65]. All the atoms were allowed to fully relax until the residual forces were less than 0.03 eV/Å except for the bottom two Ru layers that were fixed to their bulk positions. The barriers were obtained using the climbing image nudged elastic band (CI-NEB) [66] method.

3. Results and discussion

3.1. Structure and electronic properties of FeO/Ru(0001)

Although the orientation and periodicity of the FeO/Ru(0001) surface superstructure were determined experimentally, the detail structure has not been characterized yet. The bilayer FeO is terminated by O atoms, and the Moire supercell has the periodicity of 21.6 Å [14]. As indicated in Fig. 1, there are three domains of FCC, HCP, and Top within the superstructure according to the registry of the Fe atoms with

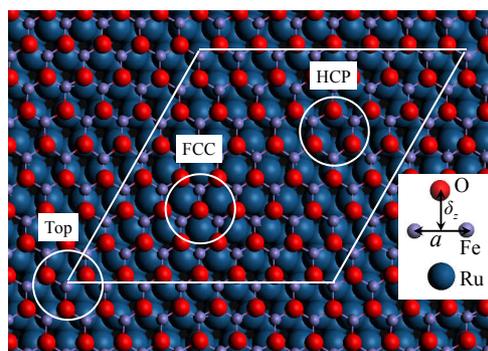


Fig. 1. Schematic Moire superstructure of (7×7)R0°-FeO(111)/(8×8)-Ru(0001) and the Top, FCC, and HCP domains inside. δ_z , the FeO bilayer rumpling (the separation between Fe and O atomic layers); a , adjacent Fe-Fe distance. Red, O atoms; blue, Fe atoms; cyan, Ru atoms.

Table 1

Calculated structural and electronic properties on the FCC, HCP, and Top domains and cell averages of FeO/Ru(0001).

Domain	a (Å)	$Z_{\text{FeO-Ru}}^a$ (Å)	δ_z (Å)	δV^b (eV)
FCC	3.00	2.76	0.76	5.88
HCP	3.42	2.36	0.12	5.33
Top	3.17	2.85	0.51	5.53
Average	3.09	2.73	0.63	5.64

^a $Z_{\text{FeO-Ru}} = (Z_{\text{Fe}} + Z_{\text{O}}) / 2 - Z_{\text{Pt}}$ is the average height of the FeO film with respect to the Pt substrate.

^b δV is the surface electrostatic potential at a height of 4.4 Å from each of the surface O atoms referenced to the Fermi energy.

respect to the Ru substrate underneath. The DFT calculation of the FeO/Ru(0001) superstructure was performed, and the optimized detail structural parameters and electronic properties are given in Table 1.

As shown in Table 1, the structural and electronic properties are different in the three domains. The FCC domain has the smallest local in-plane parameter (adjacent Fe-Fe distance), a , of 3.00 Å and the largest rumpling, δ_z , of 0.76 Å. In contrast, the HCP domain has the largest a of 3.42 Å and the smallest δ_z of 0.12 Å. The small rumpling between the O and Fe layers makes the HCP domain rather open, where iron atoms are exposed to the vacuum directly and the O atom in turn becomes coordinated to the Ru substrate with a O–Ru bond length 2.40 Å. At the same time, the FeO layer in the HCP domain has the smallest spatial separation interface $Z_{\text{FeO-Ru}}$, of 2.36 Å from the Ru substrate, while it has the largest $Z_{\text{FeO-Ru}}$ of 2.85 Å in the Top domain. The surface electrostatic potentials of the different domains correlate with the magnitude of rumpling, and the domain with a larger δ_z will have a larger surface dipole moment and electrostatic potential. Indeed, we found that the FCC domain has the largest electrostatic potential, δV , of 5.88 eV, and the HCP domain has the smallest δV of 5.33 eV. The landscape of the electrostatic potential over the Moire super cell is shown in Fig. 2. The corresponding average values of these structural and electronic properties across the whole super cell are also shown in Table 1. Furthermore, the average interfacial adhesion energy of the FeO film with the Ru substrate was calculated to be 1.11 eV/FeO.

The structural and electronic properties of FeO on Ru(0001)

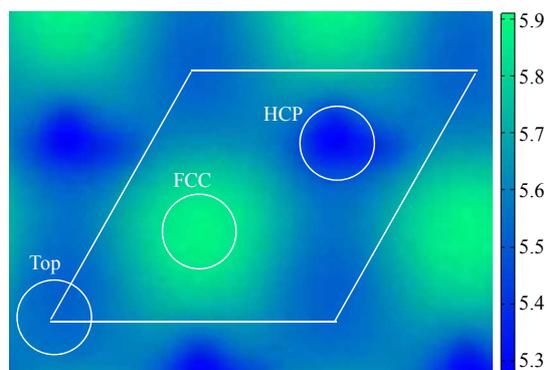


Fig. 2. Surface electrostatic potential (eV) at a height of 4.4 Å with respect to the FeO/Ru(0001) surface, with the FCC, HCP, and Top domains indicated by circles.

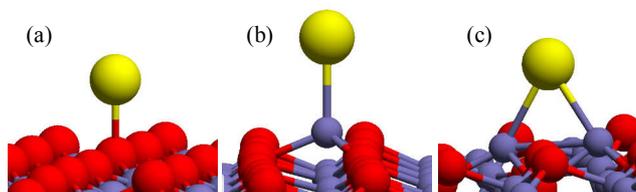


Fig. 3. Calculated stable (b,c) or metastable (a) adsorption of Au atom on FeO/Ru(0001). (a) Au adatom at O-top site; (b) Au adatom at flipped Fe-top site; (c) Au adatom at flipped Fe-bridge site.

are very different from those on Pt(111). First, the domain which has the smallest surface rumpling and potential and the largest in-plane lattice parameter on FeO/Ru(0001) is the HCP, which is in stark contrast to that on FeO/Pt(111) which is the Top. This is due to the direct binding of O atoms with Ru. The reason for the difference comes from the higher affinity of oxygen for Ru than for Pt [14]. In addition, the average interfacial adhesion energy of the FeO film on Ru (1.11 eV/FeO) is weaker than that on Pt (1.40 eV/FeO). This indicated that the interaction of Fe with Ru is weaker than with Pt, which was also reflected in the larger average $Z_{\text{FeO-Ru}}$ of 2.73 Å versus the $Z_{\text{FeO-Pt}}$ of 2.67 Å. As we will see later, Au atoms have distinct adsorption properties on FeO/Ru(0001) that are different from those on FeO/Pt(111).

3.2. Adsorption of Au atoms on FeO/Ru(0001)

The adsorption of Au atoms on the FeO/Ru(0001) surface was explored by DFT calculations. Similar to our previous work [30], Au atom adsorptions was calculated at the three sites of O-fcc (above the center of three O and Fe), O-hcp (above the center of three O and the top of Fe), and O-top in each of the FCC, HCP, and Top domains. The optimized typical adsorption configurations after full relaxation are shown in Fig. 3. The Au atom adsorption properties in each domain are given in Table 2.

In the HCP and Top domains with modest and least rumpling, we found that Au adatoms spontaneously lift low-lying Fe atoms above the O layer (flipped adsorption) without any barrier. The most stable configuration is at the Fe-top site in the

Table 2

DFT optimized configuration C_{Au} , and adsorption energy E_{Au}^a , formation energy E_{Au}^b , and Bader charge Q_{Au} of Au adatoms on FeO/Ru(0001).

Domain	FCC	HCP	Top
C_{Au}	O-top (Fe-top) ^a	Fe-bridge	Fe-top
E_{Au}^a (eV)	-0.61 (-1.09)	-1.70	-1.03
Q_{Au} (e)	0.38 (-0.36)	-0.49	-0.34
E_{Au}^b (eV)	2.42(1.93)	1.33	1.99
$C_{\text{Au-CO}}$	O-top	O-top	O-top
$E_{\text{Au-CO}}^b$ (eV)	-2.50	-2.44	-2.24
Q_{Au}^c (e)	0.75	0.56	0.57
$E_{\text{Au-CO}}^c$ (eV)	-0.07	-0.12	0.43

^aThe low lying Fe cannot be lifted by an Au adatom due to kinetic hindrance, and was lifted manually.

$C_{\text{Au-CO}}$, $E_{\text{Au-CO}}^b$, $E_{\text{Au-CO}}^c$, and Q^* are the optimized configuration, CO binding energy on Au adatom, Au-CO formation energy, and Bader charge of Au of the Au-CO carbonyls on FeO/Ru(0001), respectively.

Top domain and at the Fe-bridge site in the HCP domain. The corresponding adsorption energies E_{Au}^{s} with respect to the isolated Au atom are -1.03 and -1.70 eV, respectively, as indicated in Table 2 and Fig. 3. In the FCC domain, the Au atom could not spontaneously lift the low-lying Fe atoms, and it bonded directly with the O atom (direct adsorption) at the O-top site with an adsorption energy of -0.61 eV. However, it was found that the adsorption of the Au atom at the O-top site of FCC is metastable, and it will transit to the flipped Fe-top site by overcoming a barrier of 0.39 eV as calculated by CI-NEB with the corresponding adsorption energy of -1.09 eV.

The direct and flipped adsorption of Au adatoms reflect the special properties of the ultrathin oxide polar film. For the Au adatom directly adsorbed at the O-top site of the FCC domain, the Bader charge [65] analysis showed that it loses an electron to the Fe ion of the oxide film to become a cation with a Bader charge Q_{Au} of $0.38 |e|$, which effectively reduced the surface dipole moment and thus the electrostatic energy. For the flipped adsorption, the reverse of the Fe-O stacking manifests the structural flexibility of the ultrathin oxide film (Fig. 4). As shown in Table 2, all the Au atoms with flipped adsorption were negatively charged, $-0.39 |e|$ (FCC), $-0.44 |e|$ (HCP), and $-0.34 |e|$ (Top), due to the difference in electronegativity between Au and Fe. The primary difference between the FeO/Ru(0001) and FeO/Pt(111) systems for Au atom adsorption is that the former has an HCP domain which has a much more open structure than any of that on the latter, which results in Au coordinating with two flipped Fe atoms for FeO/Ru(0001), while coordinating with only one flipped Fe for FeO/Pt(111) [30].

The direct and flipped adsorption of Au adatoms in the different domains on FeO/Ru(0001) should be present at very low temperatures, as discussed in our previous work on Au adsorption on FeO/Pt(111) [30]. Thus the Au cation and anion will coexist. However, the formation energy of all the Au adatoms, E_{Au}^{f} , which is the Au adsorption energy with respect to the bulk counterpart, are highly endothermic. For instance, as shown in Table 2, the formation energy of the Au adatom is 1.33 , 1.93 , and 1.99 eV at the Fe-bridge site of HCP domain, and the Fe-top site of HCP and FCC domain, respectively. These values mean that at higher temperatures, these adatoms would agglomerate into clusters or large particles.

3.3. Adsorption of CO on the Au adatom

To see the influence of a reactant on the charge state, adsorption site, and the stability of the metal adatoms, the adsorption of CO on the FeO/Ru(0001)-supported Au adatoms were calculated. In each of the FCC, HCP, and Top domains, all possible configurations of Au adatom either in direct or flipped adsorption were considered. The most stable configurations of the Au-CO carbonyls and corresponding adsorption properties are shown in Table 2. Different from the Au adatoms, which prefer to be exclusively in flipped configurations and negatively charged, the carbonyls all tend to adsorb at O-top sites and in direct adsorption mode in all domains. The Au adatoms of the carbonyls all became positively charged (denoted as $\text{Au}^+\text{-CO}$

complexes) and the calculated Bader charges Q_{Au}^{s} were 0.75 , 0.56 , and 0.57 ($|e|$) in the FCC, HCP, and Top domains, respectively.

The different adsorption configurations of the $\text{Au}^+\text{-CO}$ complexes from the Au adatoms come from the strong binding between CO and the Au cations. The corresponding binding energies $E_{\text{Au-CO}}^{\text{b}}$ calculated were -2.50 , -2.44 , and -2.24 eV in the FCC, HCP, and Top domains, respectively. The stronger binding of CO with the Au cation has been well studied in the literature. The reason was attributed to the strong electrostatic interaction between CO and the Au cation [67–70]. In contrast, the binding energy $E_{\text{Au-CO}}^{\text{b}}$ of CO on the Au anion at the Fe-top site in the Top domain and the Fe-bridge site in the HCP domain ($\text{Au}^-\text{-CO}$ complexes) were calculated to be -0.71 and -0.51 eV, respectively. It is interesting to note that the transition from the Fe-bridge site ($\text{Au}^-\text{-CO}$ complexes) to the O-top site in the HCP domain ($\text{Au}^+\text{-CO}$ complexes) is facile and the calculated barrier is 0.12 eV only, as indicated in Fig. 4. These clearly showed that CO can induce the site change of the Au adatom from Fe-bridge to O-top in HCP domain, along with the reversing of the sign of the charge, which can take place even at low temperature. As a result, the Au adatoms are greatly stabilized by CO. More importantly, the formation energy of the $\text{Au}^+\text{-CO}$ complexes becomes exothermic in the FCC domain (-0.07 eV) and HCP domain (-0.12 eV).

The formation of stable $\text{Au}^+\text{-CO}$ complexes benefits from the polar nature of the FeO(111) film, which gets electrons from Au to reduce its surface polarity. For instance, as shown in Table 1, the FCC domain has a larger rumpling and thus a larger surface dipole moment than that of the Top domain, and correspondingly there is more charge transfer from Au to the Fe of the FeO film. An Au adatom in the FCC domain becomes more positive charged and has stronger binding with CO, which leads eventually to a lower formation energy of the carbonyl.

The dramatic change from Au adatoms to Au-CO carbonyls in the presence of CO has significance for catalyst stability. First, the decrease of the formation energy of the Au-CO com-

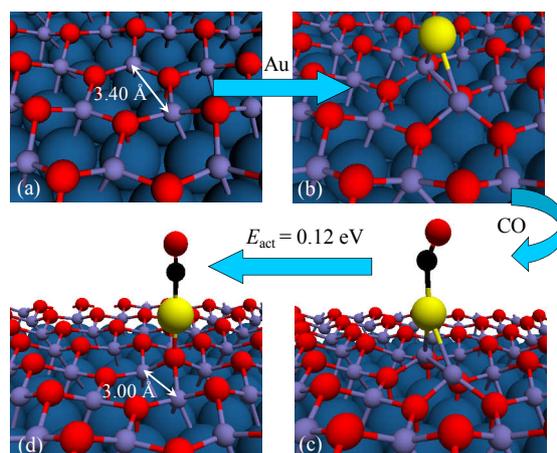


Fig. 4. Structural flexibility of FeO film and CO-induced change of Au atom adsorption site and charge. (a) HCP domain of FeO/Pt(111), with the distance of the two adjacent Fe atoms indicated; (b) After Au atom adsorption; (c) After exposure to CO; (d) Transition of the Au-CO adsorption site from Fe-bridge to O-top with a barrier of E_{act} .

plexes, compared to that of Au adatoms, would exponentially increase the concentration of the monomers responsible for Ostwald ripening of metal particles, thereby promoting catalyst sintering [45,51]. Second, the low formation energy of the Au-CO complexes can lead to the disintegration of Au particles by CO [51], which has been found on FeO/Pt(111) in the presence of CO [23]. To avoid reactant-promoted sintering and the induced disintegration of supported Au particles, one should choose the proper support to suppress the formation of these metal-reactant complexes. For example, by using a Mo-supported ultrathin MgO film, where the Au adatoms have a negative charge [71–73], the formation of Au carbonyls under CO can be prevented due to the weak binding of CO with the Au anion. In addition to stability, the CO-induced dramatic change of the adsorption site and charge of Au adatoms also has implications for catalyst characterization. Since the geometric and electronic structure of the catalyst under reaction conditions may be rather different from those under an UHV environment, the in situ characterization of the catalyst is important [49,74].

4. Conclusions

The interface structure of a bilayer FeO(111) polar film on a Ru(0001) substrate, adsorption of Au atoms on FeO/Ru(0001), and the influence of CO on the adsorption properties of the Au adatoms were studied by first principles DFT calculations. Inside the Moire supercell of FeO/Ru(0001), the order of surface rumpling is FCC > Top > HCP, which is different from the order of FCC > HCP > Top on FeO/Pt(111). The small rumpling of the HCP domain on FeO/Ru(0001) makes it rather open. The most stable adsorption of a Au adatom on FeO/Ru(0001) is at the Fe-bridge site in the HCP domain, where Au bonds with two flipped Fe atoms and is negatively charged. After exposure to CO, however, the adsorption site of Au changes from the Fe-bridge to the O-top by overcoming a small barrier of only 0.12 eV, along with a change of its charge from negative to positive to form a stable Au⁺-CO species. The CO-induced changes of the charge, adsorption site, and stability of the Au adatoms highlight the role of reactants on the activity and stability of catalysts and the importance of in situ characterization of a supported catalyst under reaction conditions.

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Graphical Abstract

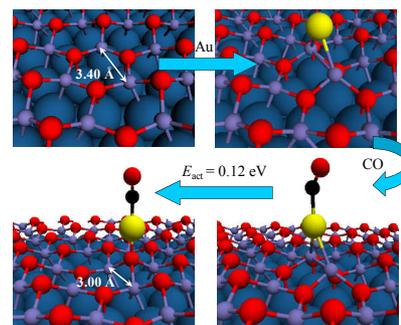
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Adsorbed CO induced change of the adsorption site and charge of Au adatoms on FeO(111)/Ru(0001)

Runhai Ouyang, Wei-Xue Li*

Dalian Institute of Chemical Physics, Chinese Academy of Sciences

The adsorption site and charge of Au adatoms on FeO(111)/Ru(0001) can be dramatically changed by CO adsorption, which highlights the importance of in situ characterization of supported metal catalyst under reaction conditions.



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