

## Direct Evidence for the Interfacial Oxidation of CO with Hydroxyls Catalyzed by Pt/Oxide Nanocatalysts

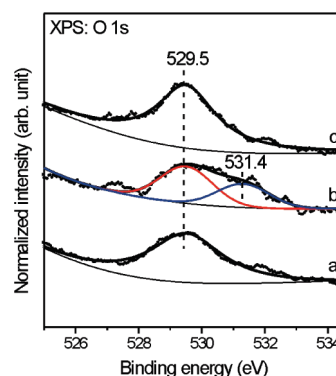
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Understanding the catalytic reaction mechanism at the molecular level is very important for the design of an efficient catalyst but still remains a great challenge. Oxide-supported platinum nanoparticles are among the promising commercial catalysts for the water-gas shift (WGS) reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ )<sup>1–3</sup> and the preferential oxidation (PROX) of CO in excess  $\text{H}_2$ <sup>4–6</sup> at low temperatures, which serve as practical strategies for reducing the CO concentration in the hydrogen stream produced from the steam reforming of various hydrocarbons in order to supply clean hydrogen fuel for polymer-electrolyte-membrane fuel cells (PEMFCs).<sup>7</sup> In the low-temperature WGS and PROX reactions catalyzed by Pt/oxide nanocatalysts, CO molecules are generally believed to chemisorb onto the Pt surface, but there is no agreement on the oxidation mechanism of  $\text{CO}_{\text{ads}}$ , a key elementary step. An associative mechanism involving the interfacial reaction of  $\text{CO}_{\text{ads}}$  on Pt with hydroxyls on the oxide surface has long been proposed to produce  $\text{CO}_2$  via surface intermediates such as formate or carboxylate in the low-temperature WGS reaction.<sup>8–10</sup> Recently, a similar mechanism was also proposed to occur in the low-temperature PROX reaction.<sup>11,12</sup> However, because of the complex nature of heterogeneous catalytic reaction systems, unambiguous experimental evidence for the above interfacial CO oxidation mechanism is still lacking. Well-defined model catalysts have been proven to be very useful in fundamental studies of heterogeneous catalytic reactions. In this work, we fabricated monolayer FeO(111) islands dispersed on a Pt(111) substrate as an inverse model catalyst. Surface hydroxyls were successfully prepared on FeO(111) and found to react readily with  $\text{CO}_{\text{ads}}$  on Pt(111) to form  $\text{CO}_2$  at low temperatures, providing for the first time direct experimental evidence for the interfacial CO oxidation mechanism.

The experiments described below were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of  $1\text{--}2 \times 10^{-10}$  mbar that was equipped with capabilities for X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and differentially pumped thermal desorption spectroscopy (TDS). The UHV chamber was also equipped with a QUAD-EV-S mini electron-beam evaporator and an MGC75 thermal gas cracker. The well-established receipt of the growth of an O-terminated epitaxial monolayer FeO(111) film on Pt(111)<sup>13</sup> was adopted to fabricate the FeO(111)/Pt(111) inverse model catalyst by oxidizing a clean Pt(111) surface partially covered by Fe in oxygen ( $P_{\text{O}_2} = 1 \times 10^{-6}$  mbar) at 850 K. The LEED pattern of the inverse model catalyst surface (Figure S1A in the Supporting Information) was the same as that of a monolayer FeO(111) film epitaxially grown on Pt(111),<sup>13</sup> proving the formation of a monolayer FeO(111) structure. The Fe  $2p_{3/2}$  and O 1s binding energies of the inverse model catalyst



**Figure 1.** (a) O 1s XPS spectra of the clean FeO(111)/Pt(111) inverse model catalyst surface. (b) The surface exposed to 10 L of D at 120 K. (c) The surface exposed to 10 L of D at 120 K and then flashed to 600 K.

(Figure S2) are located at 709.8 and 529.5 eV, respectively, also in agreement with those of FeO.<sup>13</sup>

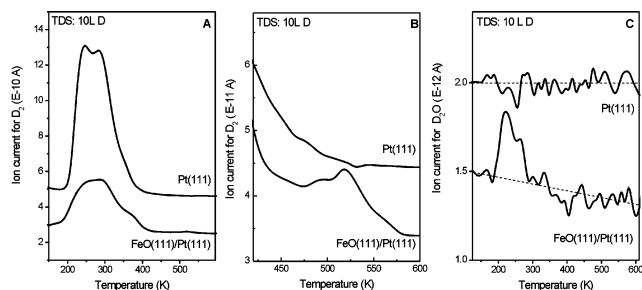
It has been reported that  $\text{CO}^{14}$  and  $\text{H}_2^{15}$  cannot chemisorb on the stoichiometric monolayer FeO(111) film, and therefore, selective chemisorption of CO and  $\text{D}_2$  on Pt(111) was employed to titrate the fraction of bare Pt(111) surface on FeO(111)/Pt(111). The CO TDS spectrum (Figure S3A) shows that in addition to the desorption trace of CO from Pt(111), a new desorption peak appeared at  $\sim 230$  K that likely arose from CO chemisorbed on  $\text{Fe}^{2+}$  exposed at the Pt–FeO interface.<sup>16</sup> Desorption of  $\text{CO}_2$  was not observed, demonstrating that  $\text{CO}_{\text{ads}}$  cannot react with oxygen in FeO(111). Only the desorption trace of  $\text{D}_2$  from  $\text{D}_{\text{ads}}$  on Pt(111) appeared in the  $\text{D}_2$  TDS spectrum (Figure S3B). By comparing the TDS peak areas of CO and  $\text{D}_2$  desorbed from bare Pt(111) on FeO(111)/Pt(111) with those from clean Pt(111), we estimated the fraction of bare Pt(111) surface on the FeO(111)/Pt(111) inverse model catalyst surface to be 32% (Figure S3C).

We found that the exposure of gas-phase atomic deuterium (D) at 120 K could form  $\text{OD}_{\text{ads}}$  on FeO(111) of FeO(111)/Pt(111). Figure 1b shows the O 1s XPS spectrum after exposure to 10 L of D at 120 K. The formation of  $\text{OD}_{\text{ads}}$  on FeO(111) is evidenced by the O 1s component with binding energy at 531.4 eV.<sup>15</sup>  $\text{OD}_{\text{ads}}$  disappeared after the surface was flashed to 600 K. The corresponding  $\text{D}_2$  TDS spectrum shows that in addition to the  $\text{D}_2$  desorption trace from Pt(111) (Figure 2A), additional tiny  $\text{D}_2$  desorption peaks between 450 and 600 K (Figure 2B) were observed. Meanwhile, a  $\text{D}_2\text{O}$  desorption peak was observed at  $\sim 235$  K (Figure 2C). It has been reported that  $\text{OH}_{\text{ads}}$  on the monolayer FeO(111) film reacts to form  $\text{H}_2$  and  $\text{H}_2\text{O}$  above 300 K.<sup>15</sup> Thus, we attributed the  $\text{D}_2$  desorption peaks between 450 and 600 K to the  $\text{OD}_{\text{ads}} + \text{OD}_{\text{ads}}$  reaction on FeO(111) and the  $\text{D}_2\text{O}$  desorption peak to the interfacial  $\text{OD}_{\text{ads}} + \text{D}_{\text{ads}}$  reaction at the Pt–FeO interface. The interfacial  $\text{OD}_{\text{ads}} + \text{D}_{\text{ads}}$  reaction to produce  $\text{D}_2$  might also occur

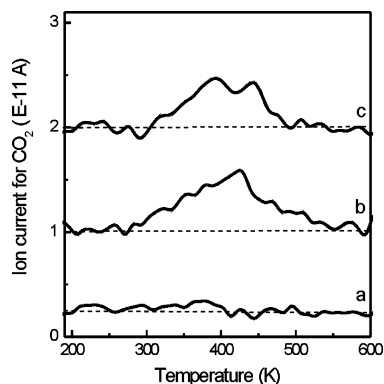
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**Figure 2.** (A)  $D_2$  TDS spectra, (B) zoom-in  $D_2$  TDS spectra between 420 and 600 K, and (C)  $D_2O$  TDS spectra of Pt(111) and FeO(111)/Pt(111) inverse model catalyst exposed to 10 L of D at 120 K. The dashed lines indicate the baselines.



**Figure 3.**  $CO_2$  TDS spectra of the FeO(111)/Pt(111) inverse model catalyst after (a) exposure to 2 L of CO, (b) 2 L of CO followed by 10 L of D, and 10 L of D followed by 2 L of CO at 120 K.

but could not be identified in our experiments. After the TDS experiment, the monolayer FeO(111) structure of FeO(111)/Pt(111) remained but was less ordered than the original one (Figure S1B).

The successful preparation of  $OD_{ads}$  on FeO(111) enabled us to further investigate the interfacial  $CO_{ads} + OD_{ads}$  reaction on the FeO(111)/Pt(111) inverse model catalyst. The FeO(111)/Pt(111) surface was exposed to 2 L of CO followed by 10 L of D at 120 K, and very intriguingly, a  $CO_2$  desorption peak centered at  $\sim 400$  K was clearly observed (Figure 3). As mentioned above,  $CO_{ads}$  chemisorbs on Pt(111) of the FeO(111)/Pt(111) surface, whereas  $OD_{ads}$  exclusively exists on FeO(111); meanwhile,  $CO_{ads}$  on Pt(111) cannot react with oxygen in FeO(111). Thus, the  $CO_2$  formation must be due to the interfacial reaction between  $CO_{ads}$  on Pt(111) and  $OD_{ads}$  on FeO(111) at the Pt–FeO interface. The formation temperature of  $CO_2$  from the interfacial  $CO_{ads} + OD_{ads}$  reaction agrees well with the reaction temperatures of low-temperature WGS and PROX reactions catalyzed by Pt/oxide nanocatalysts.<sup>1–6</sup> The chemisorption of D on bare Pt(111) of FeO(111)/Pt(111) is greatly suppressed by the preadsorbed  $CO_{ads}$  (Figure S4), and the  $D_2O$  desorption peak resulting from the interfacial  $OD_{ads} + D_{ads}$  reaction appears at 180 K (Figure S5).

The interfacial  $CO_{ads} + OD_{ads}$  reaction is not affected much by the precovered  $D_a$  on Pt(111), as a similar  $CO_2$  desorption peak was observed (Figure 3) after the catalyst was exposed to 10 L of D followed by 2 L of CO at 120 K. Therefore, the FeO(111)–Pt(111) interface that catalyzes the interfacial  $CO_{ads} + OH_{ads}$  reaction to form  $CO_2$  does not deactivate under the  $H_2$ -rich reaction conditions. This can be explained by the observation that the preadsorbed  $D_{ads}$  on Pt(111) does not significantly affect the chemisorption of CO (Figure S6). However, the repulsive interactions among coadsorbed  $CO_{ads}$  and

$D_{ads}$  on Pt(111) result in a  $D_2$  desorption peak at  $\sim 145$  K in the  $D_2$  TDS spectra (Figure S4). The  $D_2O$  desorption peak resulting from the interfacial  $OD_{ads} + D_{ads}$  reaction appears at 230 K (Figure S5).

The redox mechanism and the associative mechanism are two popular mechanisms proposed for the low-temperature WGS reaction catalyzed by Pt-based catalysts.<sup>3</sup>  $CO_{ads}$  on Pt reacts with oxygen in the oxide support in the redox mechanism<sup>17</sup> but with hydroxyls on the oxide support in the associative mechanism.<sup>8–10</sup> Our results clearly vindicate the associative mechanism for the low-temperature WGS reaction. Meanwhile, the interfacial  $CO_{ads} + OH_{ads}$  reaction to produce  $CO_2$  at low temperatures is not affected much by the precovered  $D_a$  on Pt(111), strongly implying the involvement of this interfacial reaction in the low-temperature PROX reactions catalyzed by Pt/oxide nanocatalysts. The interfacial  $CO_{ads} + OH_{ads}$  reaction previously had not been considered in the low-temperature PROX reactions catalyzed by Pt/oxide nanocatalysts<sup>6</sup> until Fukuoka et al.<sup>11</sup> recently attributed the excellent performance of Pt nanoparticles in mesoporous silica in PROX below 353 K to the attack of CO on Pt by the OH groups on mesoporous silica. The activity of Pt/oxide nanocatalysts in the PROX reaction at low temperatures could be enhanced by Fe or  $FeO_x$  additives,<sup>18–20</sup> and a recent in situ DRIFT study<sup>12</sup> indicated that the enhancement effect resulted from the oxidation of CO by hydroxyls.

In summary, the results of control experiments on the FeO(111)/Pt(111) inverse model catalyst directly prove that the interfacial  $CO_{ads} + OH_{ads}$  reaction to produce  $CO_2$  occurs readily at the Pt–oxide interface at low temperatures, providing deep insights into the reaction mechanism and active site of the important low-temperature WGS and PROX reactions catalyzed by Pt/oxide nanocatalysts at the molecular level.

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**Supporting Information Available:** Figures S1–S6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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