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Infrared Evidence of a Formate-Intermediate Mechanism over Ca-Modified Supports in Low-Temperature Ethanol Steam Reforming

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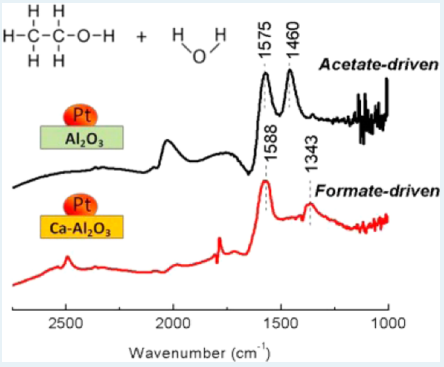
Supporting Information

ABSTRACT: An *in situ* DRIFTS study of ethanol adsorption and desorption was performed on Pt (Rh, Pd) supported on Al_2O_3 and Ca-Al_2O_3. Different from the well-known acetate-intermediate reaction mechanism observed on Al_2O_3-supported metal catalysts, formate species are exclusively observed on Pt (Rh, Pd) supported on Ca-Al_2O_3, offering a new mechanism denoted as the formate-intermediate mechanism. The key factor in determining the change in mechanism is the reduced availability of surface oxygen and the enhanced C−C breaking ability of the metal catalyst upon Ca modification. The formate-intermediate mechanism is favored in the presence of noble metals in the following order: Pt > Rh > Pd.



KEYWORDS: *ethanol steam reforming, reaction pathway, acetate, formate, Pt, Rh, Pd, Ca, Al_2O_3*

Catalytic ethanol steam reforming (ESR, eq 1) is a promising reaction for renewable hydrogen production and has been extensively explored over the past decade.[1]

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (1)$$

However, the complexity of the reaction network and the large number of intermediates presented during the reaction pose challenges in elucidating the reaction pathways.[2] A number of ESR mechanistic studies using Fourier transform infrared spectroscopy (FTIR) over supported noble metal catalysts have been conducted.[3−7] One generally proposed mechanism involves the participation of acetates via dehydrogenation and subsequent oxidation from ethoxides (eqs 2−8). Surface-adsorbed water dissociates into surface hydroxyls and/or lattice oxygen (eq 2). Ethoxides and acetates were detected at different temperatures upon ethanol adsorption (eq 3). Ethoxides can either decompose into H_2, CO, and CH_4 or undergo dehydrogenation (eq 4), producing acetaldehyde and acetyl, which may further decompose to CO and CH_4 (eq 5). The reaction of acetaldehyde and acetyl groups with lattice oxygen (eq 6) or surface hydroxyls (eq 7) leads to formation of the acetate intermediate and the final products (eq 8).[3] Herein, we denote the reaction pathway shown below as the acetate-intermediate pathway.

$$H_2O + * \rightarrow OH + H \rightarrow O + 2H \quad (2)$$

$$CH_3CH_2OH + OH(a) \rightarrow CH_3CH_2O(a) + H_2O \text{ and/or } CH_3CH_2OH \rightarrow CH_3CH_2O(a) + H(a) \quad (3)$$

$$CH_3CH_2O(a) \rightarrow CH_3CHO(a) + H(a) \rightarrow CH_3CO(a) + H_2 \quad (4)$$

$$CH_3CO(a) + H(a) \rightarrow CH_4 + CO \quad (5)$$

$$CH_3CO(a) + O(a) \rightarrow CH_3COO(a) \quad (6)$$

$$CH_3CHO(a) + OH(a) \rightarrow CH_3COO(a) + H_2 \quad (7)$$

$$CH_3COO(a) + H(a) \rightarrow CH_3(a) + CO(a) + H(a) \rightarrow CH_4 + CO_2 \quad (8)$$

Recently, the coexistence of formate and acetate species on Al_2O_3-supported Pt catalysts was reported by both Panagiotopoulou et al. and Sanchez-Sanchez et al.[7,8] Very weak IR bands of formate species were also reported over unreduced Pt/CeO_2 by Yee et al.[9] In our previous study of the Fe-promoted Rh/Ca-Al_2O_3 catalyst, formate species were proposed as an important

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intermediate in ESR.[10] Therefore, an alternative to the acetate-intermediate pathway may exist over these catalysts, which we would denote as the formate-intermediate mechanism. The Ca-modified Al_2O_3 support has proven to be beneficial in ethanol steam reforming because of the modification of the acidic versus basic properties of Al_2O_3, resulting in an increase in the surface density of active metals by weakening the metal−support interaction.[11,12] In addition, the presence of Ca reduces the extent of coke formation by reducing the metal particle size and generating more surface hydroxyls.[11,12] In this letter, to elucidate the role of catalyst support and metal in the determination of ESR pathways, we report an *in situ* DRIFTS study of ethanol adsorption and temperature-programmed desorption (TPD) on three noble metals catalysts (Pt, Rh, and Pd, each at 1 wt % loading) supported on Ca-Al_2O_3 and Al_2O_3, respectively. A formate-intermediate pathway was first proposed.

The synthesis of catalysts is described in detail in the Supporting Information. Spectroscopic experiments were performed using a Bio-Rad FT-IT 3000 MX instrument equipped with a high-temperature cell fitted with KBr windows and a mercury−cadmium−telluride (MCT-A) detector. The sample was reduced in H_2 (20 mL min^{-1}) at 473 K for 2 h and cooled in He (20 mL min^{-1}) to 303 K. Subsequently, ethanol was introduced into the cell with a He flow (50 mL min^{-1}) through a saturator for 20 min. Following this, the sample was flushed with He (50 mL min^{-1}) to remove physically adsorbed ethanol. The sample was heated to different temperatures in He (50 mL min^{-1}). Spectra were recorded at 303−673 K at a resolution of 4 cm^{-1} with typically more than 256 scans. The freshly reduced sample was used as a reference.

Figure 1a shows spectra for the adsorption of ethanol on Pt/Al_2O_3 during progressive heating. At 303 K, molecularly adsorbed ethanol and dissociative intermediates are observed. The bands at 1386 cm^{-1} [$\delta(CH_3)$ in ethanol] and 1277 cm^{-1} [δ(OH) in ethanol] correspond to molecularly adsorbed ethanol, which may bond to surface OH groups via H-bonding and/or Lewis acid sites (Al^{3+}) on the oxidic support.[13] Negative bands located at 3742 and 3700 cm^{-1} reveal the loss of surface OH groups over the Al_2O_3 support, which may interact with the molecularly adsorbed ethanol as indicated in eq 3. The presence of C−H stretching bands at 2971 cm^{-1} [$\nu_a(CH_3)$], 2935 cm^{-1} [$\nu_a(CH_2)$], and 2880 cm^{-1} [$\nu_s(CH_3)$] and C−C−O stretching of ethoxy speices at 1164 cm^{-1} indicates ethoxide species are formed via the dissociative adsorption of ethanol. Further decomposition and oxidation of adsorbed ethoxide lead to the detection of a strongly adsorbed CO band (eq 5) at 2036 cm^{-1}. The predominant bands at 1575 and 1460 cm^{-1} with an intensity ratio of 1:1 can be assigned to asymmetric and symmetric O−C−O stretching, respectively,[3] because of the presence of acetate, resulting from the dehydrogenation of ethoxide and the subsequent oxidation by lattice O or OH groups (eqs 6 and 7). In addition, three shoulders can be observed in the lower-frequency region. The peak at 1340 cm^{-1} between 303 and 473 K may be assigned to formate species.[14−16] The signals of molecularly adsorbed ethanol remain observable until 473 K but disappear at 523 K, an observation consistent with our ethanol adsorption and TPD (Figure S1 of the Supporting Information) and the literature.[3] Similarly, the intensities of bands of the ethoxide species decrease with an increase in temperature and become scarcely detectable at 523 K. On the other hand, the intensities of the CO and acetate bands increase as the temperature increases (up to 673 K), progressively. The negative bands, which are associated with hydrogen-bonded hydroxyls, in the region between 3200 and 3600 cm^{-1} become less intense as the temperature increases from 473 to 673 K. This suggests the dissociation and consumption of surface hydroxyl groups as the temperature increases. The DRIFTS results of Pt/Al_2O_3 described above are in good agreement with the literature on Pt/Al_2O_3, suggesting the acetate-intermediate mechanism.[17]

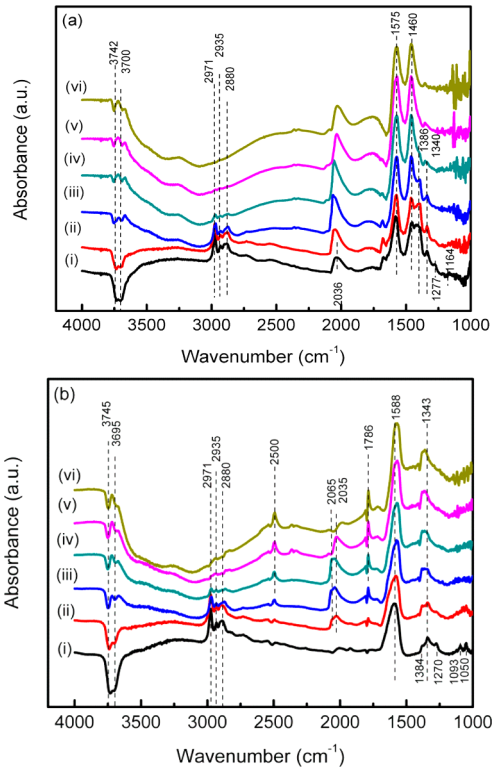

Figure 1. DRIFTS spectra at various temperatures after C_2H_5OH adsorption on (a) Pt/Al_2O_3 and (b) Pt/Ca-Al_2O_3. The spectra were recorded at (i) 303 K after ethanol adsorption followed by He purge and (ii−vi) 373, 473, 523, 573, and 673 K, respectively.

The spectra of adsorbed ethanol over Pt/Ca-Al_2O_3 are shown in Figure 1b. At 303 K, the appearance of adsorbed ethanol, ethoxides, and the negative OH bands on Pt/Ca-Al_2O_3 is similar to the appearance of those on Pt/Al_2O_3. However, there are two significant differences for Pt/Ca-Al_2O_3. First, the characteristic acetate band at 1460 cm^{-1} is not observed. Instead, two predominant bands appear at 1588 and 1340 cm^{-1}. These two bands shift to 1575 and 1360 cm^{-1}, respectively, when the temperature gradually increases from 303 to 673 K. The maximal intensity is observed at 673 K. To identify the peaks, acetic acid, formic acid, and carbon dioxide were individually adsorbed over reduced Pt/Ca-Al_2O_3 (see Figure S2 of the Supporting Information). Clearly, the peaks at 1575−1588 and 1340−1360 cm^{-1} coincide with the asymmetric and symmetric O−C−O stretching vibrations, respectively, of formate species adsorbed on the catalyst (Figure S2d of the Supporting Information).[16] In addition, the symmetric band of the O−C−O stretch at 1575 cm^{-1}, which has one-third of the intensity of its asymmetric band at 1360 cm^{-1}, further affirms the presence of formate species at higher temperatures.[18] This is the first time that formate species have been clearly identified.

The second noticeable difference between Pt/Al_2O_3 and Pt/Ca-Al_2O_3 is that the CO band is not evident on Pt/Ca-Al_2O_3 at

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303 K. CO adsorption is associated with the dissociation of ethoxide species. The smaller amount of adsorbed CO on Pt/Ca-Al_2O_3 at 303 K suggests that ethoxide species are more stable on Pt/Ca-Al_2O_3 than on Pt/Al_2O_3. This is because the Ca-modified catalysts have a higher affinity for water adsorption and the adsorbed water is found to be able to stabilize the ethoxide species at room temperature.[19] Progressive heating of the sample leads to the loss of molecularly adsorbed ethanol as well as ethoxide species. This is seen in the decreasing intensity of the corresponding bands at 1384, 1270, 1095, 1054, 2971, 2935, and 2880 cm^{-1} (Figure 1b). It is observed that the loss of ethoxide runs parallel to the increase in CO adsorption on Pt/Ca-Al_2O_3 between 373 and 523 K. Between 373 and 523 K, two vibration modes of linearly adsorbed CO are observed: CO adsorbed on partially oxidized $Pt^{\delta+}$ [υ(CO) = 2065 cm^{-1}] and CO adsorbed on reduced Pt^0 particles [υ(CO) = 2035 cm^{-1}].[7] The presence of partially oxidized $Pt^{\delta+}$ could be due to the oxidation of Pt^0 by surface oxygen deriving from dissociation of CO or H_2O. The intensity of υ(CO) bands starts to decrease at ≥573 K, leaving a weak band at 2000 cm^{-1}. Similar to the data in Figure 1a, the intensity of the bands in the region between 3200 and 3600 cm^{-1} decreases at 473−673 K, indicating the dissociation and consumption of surface hydroxyls as the temperature increases. At 473 K, two new bands at 2500 and 1786 cm^{-1} are observed. These two bands are not observed in Figure 1a, which indicates that these bands are associated with the presence of Ca species. Several authors have assigned the peak at 1786 cm^{-1} to the υ(CO) mode of adsorbed acetaldehyde.[19,20] However, it is shown through ethanol adsorption and TPD in Figure S1a of the Supporting Information that acetaldehyde decomposes completely at approximately 550 K. Therefore, the peak at 1786 cm^{-1} is unlikely to be related to adsorbed acetaldehyde because the marked increase in its intensity occurs between 473 and 673 K. Instead, it is more reasonable to assign the two peaks to the H−OC and HC═O stretches of adsorbed HCO species, respectively.[21,22] The formation of these species will require the cleavage of the C−C bond with the assistance of active metal sites, and it cannot occur over the Ca-Al_2O_3 support alone, especially at low temperatures.

Early surface science study of the adsorption of ethanol on Ni(111) and Pt surfaces revealed that the adsorption of ethanol on Ni(111) or Pt surfaces is dissociative following the (i) O−H, (ii) C_α−H, (iii) C−C, (iv) C_β−H bond scission sequence.[23,24] Recent density functional theory (DFT) calculation of ESR on Pt indicated that the activation energy for C−C scission decreases with increasing levels of ethanol dehydrogenation.[25] C−H bond scission leads to a coordinatively unsaturated ketenyl or acetyl carbon atom, which may then be stabilized by forming metal−carbon bonds, causing a weakening of the C−C bond. The DFT calculation also showed that oxidative dehydrogenation by surface OH groups is energetically more favorable than thermal decomposition of ethanol without the assistance of surface OH groups. The oxidative dehydrogenation is not remarkable on Ca-free Pt/Al_2O_3 catalysts because of the low coverage of adsorbed OH. However, oxidative dehydrogenation (e.g., C_β−H) and thus C−C cracking are expected on the Ca-promoted Pt/Al_2O_3 catalyst because of the presence of abundant OH groups. Therefore, C−C bond scission may occur on Ca-Al_2O_3-supported Pt catalysts, leading to the generation of adsorbed HCO (eq 9). The C═O carbonyl vibration is typically observed at 1786 cm^{-1} in Figure 1b, while the H−C stretching vibration is shifted to 2500 cm^{-1}. This is understandable if the hydrogen atom of HCO is bonded to adsorbed oxygen on Ca-Al_2O_3, forming a CaO···H···C═O species. The downshift of the C−H vibration (to 2715 cm^{-1}) caused by H-bonding was previously reported by Iwasawa et al. for the bidentate formate.[15] In the presence of abundant surface OH groups, the adsorbed CO or HCO species on the catalyst surface can be converted to formate species HCOO (eqs 10−11). The HCOO intermediate may undergo either dehydration (to CO) or dehydrogenation (to H_2 and CO_2) (eq 12), depending on the structure of the formate. Previous studies showed that bidentate formate favors dehydrogenation while monodentate leads to dehydration.[14,15] Surface-adsorbed water was reported to assist 100% dehydrogenation of formate on oxide-supported Rh catalysts.[15] Obviously, the formate species on Pt/Ca-Al_2O_3 with characteristic COO vibrations at 1575 and 1360 cm^{-1} (Figure 1b and Figure S2e of the Supporting Information) are bidentate, and the presence of adsorbed water (or surface OH groups) can further enhance dehydrogenation of the formate intermediates, producing CO_2 and H_2 upon heating (eq 12).

At present, spectroscopic evidence clearly shows that the modification of alumina by calcium has altered the reaction pathway of ESR from the one mediated by acetates (acetate-intermediate) over Pt/Al_2O_3 to the one aided by formate species (formate-intermediate) over Pt/Ca-Al_2O_3. Therefore, our results unravel a new mechanism for ethanol reforming over Ca-Al_2O_3-supported Pt catalysts, the formate-intermediate reaction pathway:

$$H_2O + * \rightarrow OH + H \rightarrow O + 2H \quad (2)$$

$$CH_3CH_2O(a) \rightarrow CH_3CHO(a) \rightarrow CH_3(a) + HCO(a) \quad (9)$$

$$HCO(a) + * \leftrightarrow CO(a) + H(a) \text{ or}$$
$$HCO(a) + OH(a) \rightarrow CO(a) + H_2O \quad (10)$$

$$OH(a) + CO(a) \leftrightarrow HCOO(a) + * \text{ or}$$
$$O(a) + HCO(a) \rightarrow HCOO(a) \quad (11)$$

$$HCOO(a) + H(a) \leftrightarrow CO_2 + H_2 \quad (12)$$

The formate-intermediate pathway is also observed over Rh and Pd catalysts. On Rh/Ca-Al_2O_3 (Figure 2a), adsorption bands [υ_a(O−C−O) = 1572 cm^{-1}, and υ_s(O−C−O) = 1380 cm^{-1}] at 473 K are attributed to formate species, and the intensities of these bands gradually increase as the temperature increases. The two bands at 2030 and 1830 cm^{-1} correspond to linear and bridge-bonded Rh-CO, respectively. At high temperatures (>573 K), the depletion of hydroxyl and the appearance of HCO species (H−OC and HC═O stretches at 2495 and 1784 cm^{-1}, respectively) are similarly observed in Figure 1b. On Pd/Ca-Al_2O_3 (Figure 2b), the presence of formate species is evidenced by an intense band at 1609 cm^{-1} along with a band located at 1339 cm^{-1}.[26] However, the IR band at 1930 cm^{-1}, which can be attributed to bridge-bonded CO, is rather weak on Pd.[27] TPD of ethanol over Pd/Ca-Al_2O_3 indicates the desorption of CO and H_2 at 657 K, whereas CO is essentially converted to CO_2 over Pt and Rh catalysts (Figure S1 of the Supporting Information). DFT calculations showed that the ability of Pd to adsorb CO is not as good as those of other noble metals such as Pt, Rh, Ru, Os, and Ir, which could probably explain why Pd is less active for the catalytic ESR

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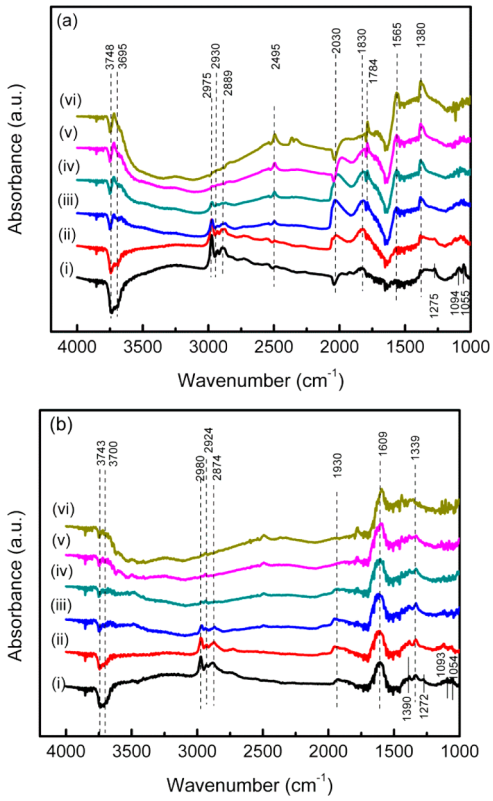


Figure 2. DRIFTS spectra at various temperatures after C_2H_5OH adsorption on (a) Rh/Ca-Al_2O_3 and (b) Pd/Ca-Al_2O_3. The spectra were recorded at (i) 303 K after ethanol adsorption followed by He purge and (ii–vi) 373, 473, 523, 573, and 673 K, respectively.

reaction in this contribution (Table S1 of the Supporting Information).[28] Here, the reaction mechanism over Rh/Ca-Al_2O_3 and Pd/Ca-Al_2O_3 is similar to that of Pt/Ca-Al_2O_3, i.e., formate-intermediate pathway. The weak IR bands belonging to formate species and adsorbed CO suggest poorer WGSR activity on Rh and Pd than on Pt catalysts, an observation that is in agreement with the literature.[29]

As indicated above, over the Ca-Al_2O_3-supported Pt, Rh, and Pd catalysts, ESR follows the formate-intermediate pathway, which suggests that formate formation is independent of the nature of the active metal. This is consistent with the conclusion of Erdöhelyi et al., who observed the formation of surface acetates over Al_2O_3-supported Rh, Ir, Ru, Pd, and Pt catalysts.[3] Therefore, the change from the acetate- to formate-intermediate reaction pathway in this study is solely related to the changes in the surface properties of the support induced by Ca addition.

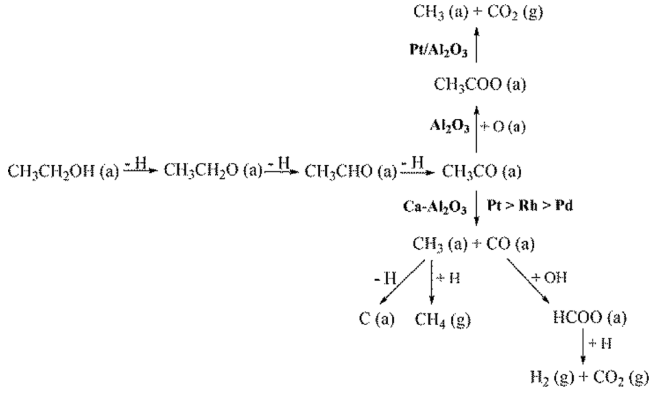
Formation of acetates from ethanol adsorption has been widely reported over various oxides, such as Al_2O_3, MgO, and CeO_2.[6,30−32] A structural change from an ethoxide to an acetate species occurs via dehydrogenation to form an acyl group that is subsequently oxidized to form acetate. Yee et al. studied ethanol adsorption over unreduced CeO_2, reduced CeO_2, and Pd/CeO_2.[6] Their results show that surface oxygen atoms on unreduced CeO_2 are responsible for acetate formation. On the other hand, the formation of acetate is not observed on the reduced CeO_2 because of the depletion of surface oxygen atoms. The presence of Pd facilitates partial reduction of CeO_2, which also leads to no acetate formation over reduced Pd/CeO_2. Therefore, the high availability of oxygen atoms on the support favors the oxidation of carboxyl carbon to acetate.[30] Similar to the results reported by Yee et al., on the surfaces of Ca-free Al_2O_3 and Pt/Al_2O_3 catalysts, there are large numbers of surface oxide ions in close interaction with the adsorbed ethoxide/acetaldehyde (located at Al^{3+} Lewis acidic centers or Pt sites at the metal−oxide interface), favoring the formation of acetate species as evidenced in Figure 1a and the literature.[3,6,31,33]

The presence of Ca induced significant changes in the surface properties, thereby altering the reaction pathway.[11,12] Our previous DRIFTS studies clearly showed that ethoxide was not formed at 673 K while acetates were observed over Al_2O_3. In contrast, ethoxide species were detected over Ca-Al_2O_3 at 673 K, without observable bands attributed to either acetate or formate species. Characterization of the Ca-Al_2O_3 surface showed a large amount of adsorbed water on the surface of the sample.[11] These species and the presence of Ca might block surface oxygen sites that closely interact with the active sites, hindering the formation of acetate species.[33] In addition, on the basis of DFT calculations, the presence of extra OH groups can facilitate the formation of CO_2 through COO−H bond breaking, which has almost no energy barrier.[34]

It is worth noting that the formate species can be observed only in the presence of an active metal on Ca-Al_2O_3. Previous studies of a Ni catalyst supported on Ca-modified Al_2O_3 have shown that Ca modification on Al_2O_3 prevents the formation of nickel aluminates, resulting in higher Ni concentrations on the surface of the catalyst. In addition, an electron density near the Fermi level due to the contribution of Ni 3d is enhanced due to the presence of Ca.[12] Similarly, on the Pt/Ca-Al_2O_3 catalyst, Ca can increase the electronic density of the catalyst. This electronic modification on Pt will enhance the adsorption of the alcohol on the catalyst, causing an increase in the stability of the ethoxides as shown by DRIFTS.[32] On the other hand, the presence of abundant surface OH groups can facilitate the dehydrogenation of adsorbed ethanol, reducing the activation energy of C−C bond cracking. Hence, ethanol adsorption and reaction on Ca-Al_2O_3-supported Pt catalysts may follow the new formate-intermidate reaction pathway shown in Scheme 1. HCO is first formed and reacts with adjacent OH or O, generating formate species (HCOO) on the surface (eq 11). The HCOO intermediates further undergo dehydrogenation to generate H_2 and CO_2 (eq 12).

In conclusion, the reaction pathways of ESR on noble metals (Pt, Rh, and Pd) supported on Al_2O_3 and Ca-Al_2O_3 were

Scheme 1. Reaction Pathways of Ethanol over Al_2O_3- and Ca-Al_2O_3-Supported Noble Metals



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thoroughly investigated using *in situ* DRIFTS, ethanol TPD, and steady-state catalytic testing. The ESR pathway over Pt/Al_2O_3 involves the formation of acetates. In contrast, the presence of Ca in the Pt/Ca-Al_2O_3 catalyst alters the reaction pathway from the acetate- to formate-intermediate pathway. This is due to the deficiency of surface oxygen as well as an increase in the Fermi level upon Ca modification. The proposed reaction pathways are illustrated in Scheme 1. This is the first time that the formate-intermediate reaction pathway for ESR is clearly revealed by an *in situ* FTIR study.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details; DRIFTS spectra of ethanol, acetic acid, formic acid, and CO_2; catalytic activity; and temperature-programmed desorption of ethanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Yamazaki, T.; Kikuchi, N.; Katoh, M.; Hirose, T.; Saito, H.; Yoshikawa, T.; Wada, M. *Appl. Catal., B* **2010**, *99*, 81−88.
(2) Mattos, L. V.; Jacobs, G.; Davis, B. H.; Noronha, F. B. *Chem. Rev.* **2012**, *112*, 4094−4123.
(3) Erdőhelyi, A.; Raskó, J.; Kecskés, T.; Tóth, M.; Dömök, M.; Baán, K. *Catal. Today* **2006**, *116*, 367−376.
(4) Jacobs, G.; Keogh, R. A.; Davis, B. H. *J. Catal.* **2007**, *245*, 326−337.
(5) Song, H.; Bao, X.; Hadad, C.; Ozkan, U. *Catal. Lett.* **2011**, *141*, 43−54.
(6) Yee, A.; Morrison, S. J.; Idriss, H. *J. Catal.* **1999**, *186*, 279−295.
(7) Panagiotopoulou, P.; Verykios, X. E. *Int. J. Hydrogen Energy* **2012**, *37*, 16333−16345.
(8) Sanchez-Sanchez, M. C.; Navarro Yerga, R. M.; Kondarides, D. I.; Verykios, X. E.; Fierro, J. L. G. *J. Phys. Chem. A* **2010**, *114*, 3873−3882.
(9) Yee, A.; Morrison, S. J.; Idriss, H. *J. Catal.* **2000**, *191*, 30−45.
(10) Chen, L.; Choong, C.; Zhong, Z.; Huang, L.; Ang, T. P.; Hong, L.; Lin, J. *J. Catal.* **2010**, *276*, 197−200.
(11) Choong, C.; Huang, L.; Zhong, Z.; Lin, J.; Hong, L.; Chen, L. *Appl. Catal., A* **2011**, *407*, 155−162.
(12) Choong, C.; Zhong, Z.; Huang, L.; Wang, Z.; Ang, T. P.; Borgna, A.; Lin, J.; Hong, L.; Chen, L. *Appl. Catal., A* **2011**, *407*, 145−154.
(13) Raskó, J.; Dömök, M.; Baán, K.; Erdőhelyi, A. *Appl. Catal., A* **2006**, *299*, 202−211.
(14) Lin, J.; Neoh, K. G.; Teo, W. K. *J. Chem. Soc., Faraday Trans.* **1994**, *9*, 355−362.
(15) Shido, T.; Asakura, K.; Iwasawa, Y. *J. Catal.* **1990**, *122*, 55−56.
(16) Solymosi, F.; Koós, Ã.; Liliom, N.; Ugrai, I. *J. Catal.* **2011**, *279*, 213−219.
(17) Dömök, M.; Tóth, M.; Raskó, J.; Erdőhelyi, A. *Appl. Catal., B* **2007**, *69*, 262−272.
(18) Hertl, W.; Cuenca, A. M. *J. Phys. Chem.* **1973**, *77*, 1120−1126.
(19) Idriss, H.; Diagne, C.; Hindermann, J. P.; Kiennemann, A.; Barteau, M. A. *J. Catal.* **1995**, *155*, 219−237.
(20) Silva, A. M.; Costa, L. O. O.; Barandas, A. P. M. G.; Borges, L. E. P.; Mattos, L. V.; Noronha, F. B. *Catal. Today* **2008**, *133−135*, 755−761.
(21) Raskó, J.; Kiss, J. *Appl. Catal., A* **2005**, *287*, 252−260.
(22) Cabilla, G. C.; Bonivardi, A. L.; Baltanás, M. A. *Appl. Catal., A* **2003**, *255*, 181−195.
(23) Gates, S. M.; Russell, J. N., Jr.; Yates, J. T., Jr. *Surf. Sci.* **1986**, *171*, 111−134.
(24) Mavrikakis, M.; Barteau, M. A. *J. Mol. Catal. A: Chem.* **1998**, *131*, 135−147.
(25) Sutton, J. E.; Panagiotopoulou, P.; Verykios, X. E.; Vlachos, D. G. *J. Phys. Chem. C* **2013**, *117*, 4691−4706.
(26) Borchert, H.; Jürgens, B.; Zielasek, V.; Rupprechter, G.; Giorgio, S.; Henry, C. R.; Bäumer, M. *J. Catal.* **2007**, *247*, 145−154.
(27) Maroto-Valiente, A.; Rodríguez-Ramos, I.; Guerrero-Ruiz, A. *Thermochim. Acta* **2001**, *379*, 195−199.
(28) Liu, W.; Zhu, Y. F.; Lian, J. S.; Jiang, Q. *J. Phys. Chem. C* **2007**, *111*, 1005−1009.
(29) Panagiotopoulou, P.; Kondarides, D. I. *Catal. Today* **2006**, *112*, 49−52.
(30) Greenler, R. G. *J. Chem. Phys.* **1962**, *37*, 2094−2100.
(31) Kagel, R. O. *J. Phys. Chem.* **1967**, *71*, 844−850.
(32) Kagel, R. O.; Greenler, R. G. *J. Chem. Phys.* **1968**, *49*, 1638−1647.
(33) Evans, H. E.; Weinberg, W. H. *J. Chem. Phys.* **1979**, *71*, 1537−1542.
(34) Zhang, J.; Zhong, Z.; Cao, X.; Hu, P.; Sullivan, M.; Chen, L. *ACS Catal.* **2014**, *4*, 448−456.