

Influence of ligand structures on methanol electro-oxidation by mixed catalysts based on platinum and organic metal complexes for DMFC

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Abstract

In order to investigate the influence of mixing organic metal complexes with various metal coordination structure on Pt/C catalyst for methanol oxidation reaction (MOR) in acidic media, *N,N'*-mono-8-quinoly-*o*-phenylenediamine (mqph), *N,N'*-bis(anthranilidene)ethylenediamine (anthen) and *N,N'*-bis(salicylidene)ethylenediamine (salen), coordinating to Co(II) and Ni(II), were examined as the model compounds. M(mqph), M(anthen) and M(salen) have MN₃, MN₄ and MN₂O₂ moiety as the catalytic active sites, respectively. Pt–M(complex)/C mixed catalysts were prepared by depositing the mixture of Pt tetra-ammine chloride and each organic metal complex with various mixing ratio (w/o) on graphite powder and then heat-treating at 600 °C in Ar atmosphere. The Pt–M(complex)/C samples were put on a glassy carbon disk electrode, and tested for electrochemical MOR in 1 mol dm⁻³ CH₃OH + 0.05 mol dm⁻³ H₂SO₄ aqueous solutions at 25 °C. The mixed catalysts, especially Pt–Ni(mqph)/C and Pt–Co(mqph)/C, were found to enhance the MOR and exhibited higher catalytic activities than Pt/C, although each organic metal complex solely showed no catalytic activity. The catalytic ability was enhanced by mixing up to 50/50 (Pt–M(complex)) mixing ratio for the Co(mqph) and up to 80/20 mixing ratio for the Ni(mqph). Larger amounts of M(complex) resulted in a decrease in the catalytic activities. These results indicate that the organic metal complexes, especially M(mqph), promote effectively the electrochemical MOR on Pt/C catalyst, the degree of which depends strongly on the ligand structure. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectra (XAS) for the Pt–M(complex)/C mixed catalysts showed that the metal coordination structures of organic metal complexes are partially retained on the graphite powder even after the severe heat-treatment at 600 °C in Ar atmosphere. Ab initio calculations for the organic metal complexes exhibited that the Ni metal site of the Ni(mqph) interact with OH⁻ group more strongly than those of the other organic metal complexes. This fact suggests that the Pt–M(mqph)/C electro-oxidizes a byproduct CO absorbed on Pt by “bifunctional effect” in a similar way as Pt–Ru alloy catalysts do in promoting the effective electrochemical MOR.

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Keywords: DMFC; Anode; Methanol electro-oxidation; Platinum; Organic metal complex based co-catalyst; Ab initio calculation

1. Introduction

In recent years, direct methanol fuel cells (DMFCs) have received increasing attention as various power sources for

portable applications such as cellular phones, PDAs, laptop computers, etc. [1–3]. Many studies have been done to realize DMFCs with higher performances. However, for actual application there are some issues, i.e. (i) a high activation energy barrier of methanol electro-oxidation on the anode, (ii) poisoning of Pt catalyst by a byproduct carbon monoxide (CO) generated during the MOR on the anode and (iii) methanol crossover through electrolyte membranes such as Nafion, etc. Especially, (i) and (ii) are causing a high overpotential that should be coped with by increasing the loading amount of Pt as the anode catalyst.

In order to overcome these issues, various approaches have been implemented and the most common approach is to use binary alloy catalysts such as Pt–Ru, Pt–Sn Pt–Mo, etc. [4–12]. Especially, Pt–Ru alloy catalyst exhibits an effective electro-

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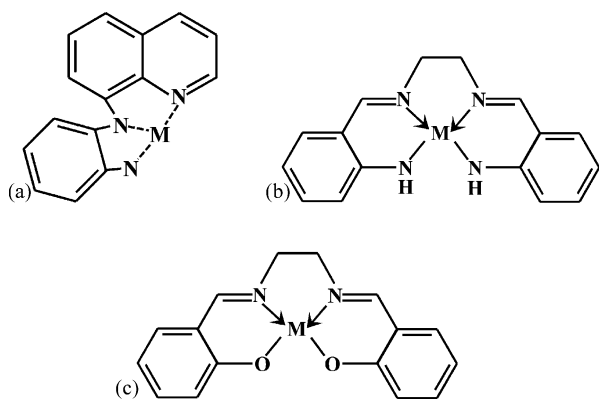
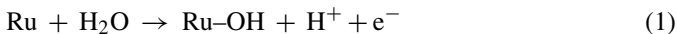


Fig. 1. Chemical structure of organic metal complexes tested. (a) M(mqph), (b) M(anthen) and (c) M(salen). Coordination by acetate ligands during the synthesis is omitted.

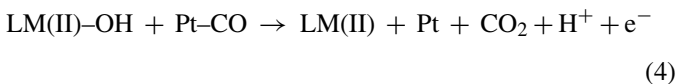
chemical MOR. In this case, it is well known that Ru easily adsorbs and dissociates water in the electrolyte and provides a Ru–OH that oxidizes the CO on Pt by the following scheme [5,6,8]:



On the other hand, macrocyclic complexes are believed to act as redox mediators that take part in the oxidation of CO by generating oxidizing species as follows [13]:



where L stands for the ligand (macrocycle) and M stands for the metal.



Bett et al. [14] have successfully carried out a study using macrocycles as co-catalysts to Pt for electrochemical MOR. They found that Pt co-catalyzed with ruthenium tetramethylcyclam enhances the MOR in 1 M H₂SO₄ at 60 °C. In our recent studies [15–17], we have also examined Pt catalysts co-catalyzed with various organic metal complexes, M(mqph), M(anthen) and M(salen) (M = Co, Ni, Fe, Mo, Mn, etc.) (Fig. 1), and demonstrated that mixing organic metal complexes with Pt catalyst noticeably enhances the electrochemical MOR in acidic media. However, the mechanism of its enhancement and the dependence on the structures of organic metal complexes were still left unresolved.

In this study, we intend to examine the mechanism of the MOR enhancement by the organic metal complexes by selecting the co-catalysts M(mqph), M(anthen) and M(salen) as the model compounds (M = Co or Ni). As molecular structure characterization, X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) are conducted and the results are discussed in relation to the electrochemical MOR performances of the catalysts. The mechanism is also substantiated by ab initio

calculations for the optimum structure and energetic of organic metal complexes as the reaction sites for intermediates.

2. Experimental

2.1. Synthesis of organic metal complexes

N,N'-mono-8-quinolyl-*o*-phenylenediamine (mqph) was synthesized as reported previously [16]. Equimolar amounts of the mqph ligand and each metal (Co or Ni) acetate salt were mixed in ethanol in a glass flask for 1 h at room temperature under N₂ atmosphere. The resulting solution was concentrated and refrigerated to obtain the precipitated organic metal complexes. The complex samples were purified by re-crystallization. *N,N'*-bis(salicylidene)ethylenediamine (salen) and *N,N'*-bis(anthranilidene) ethylenediamine (anthen) of Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan) were used without further purification.

2.2. Preparation of Pt–M(complex)/C mixed catalysts

Platinum tetra-ammine chloride Pt(NH₃)₄Cl₂·*x*H₂O and each organic metal complex were mixed in various weight ratio as the precursors of Pt–M(complex)/C mixed catalysts. The Pt–M(complex)/C mixed catalysts were prepared by mixing 10 mg of the mixed precursors and 40 mg of graphite powder of Aldrich (1–2 μm) in 0.5 cm³ of ethanol in a mortar, drying in air at 80 °C for 1 h and then heat-treating in Ar atmosphere at 600 °C for 2 h in a furnace. The heat-treatment condition was determined in our previous study [17], where the condition gave the highest MOR performances for all the Pt–M(complex) mixed catalysts. The electrochemical MOR activities increased with increasing the temperature of heat-treatment up to 600 °C and higher temperature caused a decrease in the MOR activities.

2.3. Electrochemical MOR measurement

The electrochemical MOR measurements were performed with the same methods described previously [15–17]. The working electrode was prepared by using the obtained Pt–M(complex)/C mixed catalysts and Nafion solution. A 5 mg of the mixed catalysts was mixed with 100 mg of 5% Nafion solution (Aldrich) together with 0.1 cm³ of ethanol, to get an ink of the mixture. A 0.01 cm³ of this mixture was coated to the disk electrode (6 mm diameter) made of glassy carbon and then the solvent was evaporated. The amount of the mixed catalyst was fixed at 1.8 × 10^{−4} g cm^{−2} on the disk electrode.

Linear sweep voltammogram (LSV) was measured to evaluate the electrochemical MOR properties for the working electrodes by using a three-electrode glass cell in 0.05 mol dm^{−3} H₂SO₄ with and without 1 mol dm^{−3} CH₃OH at 25 °C under the deaerated condition with N₂ gas. The counter and the reference electrodes were Pt foil and saturated calomel electrode (SCE), respectively. The potential sweep rate was 1 mV s^{−1} and the potential range was −200 to 1000 mV versus SCE. The potentials hereafter are recalculated to RHE scale by adding 316 mV.

2.4. Structural and chemical state analyses for Pt–M(complex)/C mixed catalysts

The chemical states of Pt, Co and Ni in the Pt–M(complex)/C mixed catalysts before and after the heat-treatment at 600 °C in Ar atmosphere were evaluated with a Perkin-Elmer model PHI5600 XPS apparatus with monochromic Al K_{α} of 2 mm ϕ at 14 kV, 100 W.

The coordination around Co ion and its valence state in the Pt–Co(complex)/C before and after the heat-treatment were examined by XAS technique. Co K-edge XAS spectra were performed by transmission mode at PF BL-7C beam-line (High Energy Accelerator Research Organization in Tsukuba, Japan).

2.5. Interaction energy calculations

Gaussian 03 program [18] was used for ab initio molecular orbital calculations. The geometries of organic metal complexes interacting with and without OH[−] or CO were optimized at the HF/6-31G* level. The optimized geometries were used for the calculations of lowest unoccupied molecular orbital (LUMO)

and the intermolecular interaction energies of organic metal complexes with OH[−] or CO. The interaction energies were calculated at the MP2/6-311 + G** level. The basis set superposition error (BSSE) [19] was corrected for all calculations using the counterpoise method [20].

3. Results and discussion

3.1. Electrochemical MOR by Pt–M(complex)/C mixed catalysts

Fig. 2 shows the LSVs of MOR on Pt–M(complex)/C mixed catalysts (Pt–M(complex) mixing ratio = 50/50) measured in 0.05 mol dm^{−3} H₂SO₄ + 1 mol dm^{−3} CH₃OH at 25 °C, where M = Co, Ni and the ligand is varied for mqph, anthen and salen. The currents are normalized against the Pt mass of the catalysts. Almost all the co-catalysts induced lower overpotential and higher current values for the electrochemical MOR than the Pt/C catalyst. Especially, the Pt–Co(mqph)/C and the Pt–Ni(mqph)/C mixed catalysts exhibited the highest electro-catalytic activities among other organic metal complexes. These results suggest

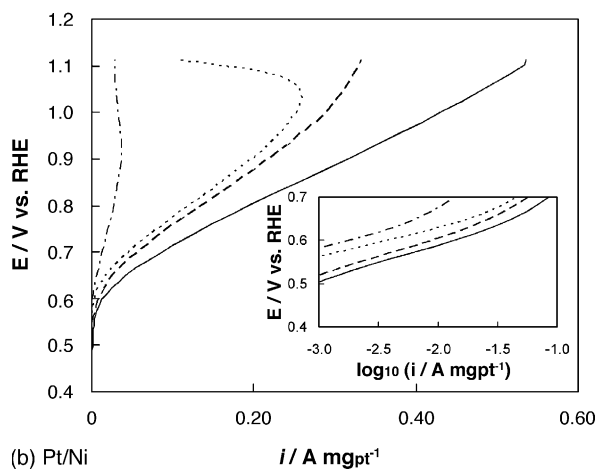
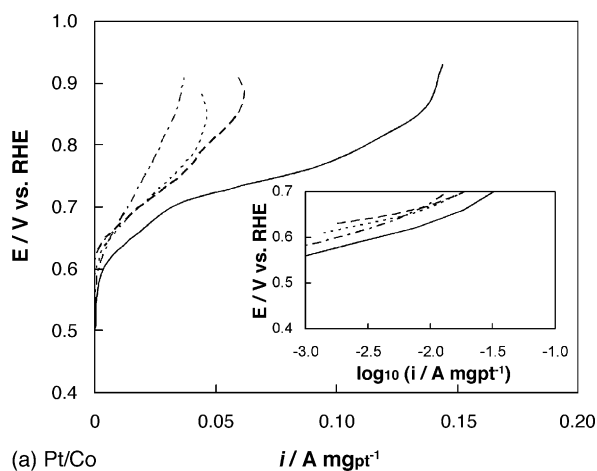


Fig. 2. LSVs for Pt–M(complex)/C mixed catalysts (M = Co; Ni, mixing ratio = 50/50) in 0.05 mol dm^{−3} H₂SO₄ + 1 mol dm^{−3} CH₃OH at 25 °C. Potential scan rate: 1 mV s^{−1}. —, mqph; ---, anthen; ···, salen; ---, 10 wt.% Pt/C (Aldrich).

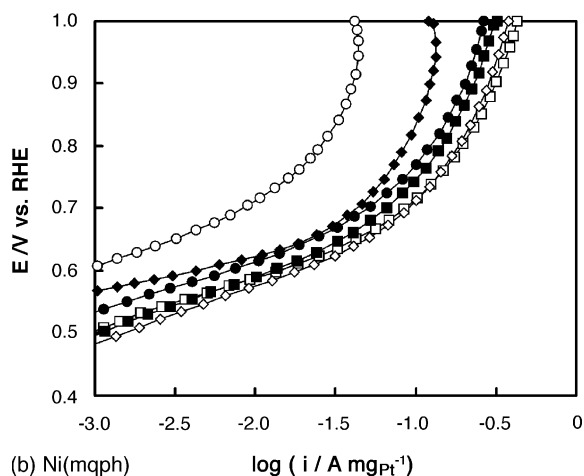
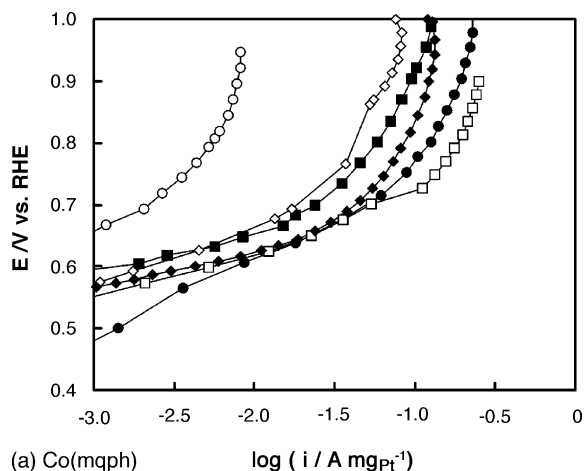


Fig. 3. LSVs for the Pt–M(mqph)/C mixed catalysts with various mixing ratios in 0.05 mol dm^{−3} H₂SO₄ + 1 mol dm^{−3} CH₃OH at 25 °C. Potential scan rate: 1 mV s^{−1}. Mixing ratio: (○), 20/80; (●), 40/60; (□), 50/50; (■), 60/40; (◇), 80/20; (◆), 100/0.

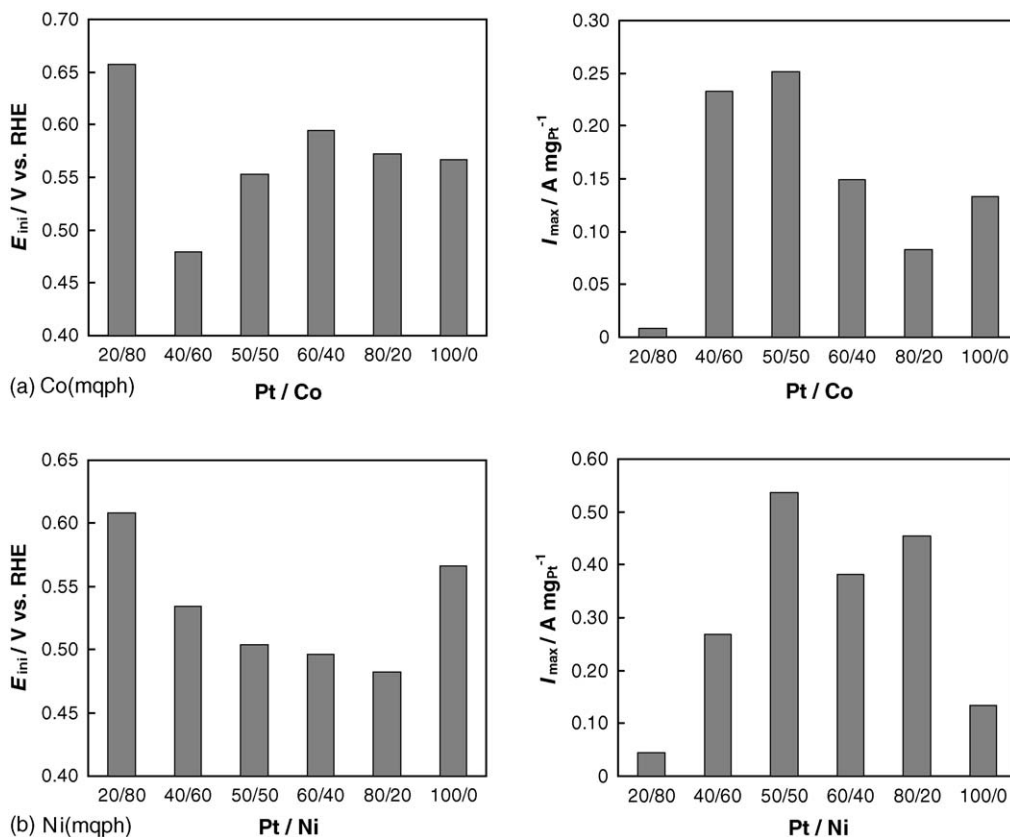


Fig. 4. The initial potential E_{ini} temporally defined at anodic current of $1 \text{ mA mg}_{\text{Pt}}^{-1}$ and the current maximum value I_{max} for the MOR using Pt–M(mqph)/C mixed catalysts against the mixing ratio.

that the catalytic activity of Pt/C catalyst was enhanced by mixing the organic metal complexes and the effect depends on the ligand structures.

In order to investigate the electro-catalytic effect due to the organic metal complexes in more detail, the mixing ratio was changed for both Pt–Co(mqph)/C and Pt–Ni(mqph)/C co-catalysts and their MOR activity was examined. The results of LSVs are shown in Fig. 3. The electro-catalytic activities increased by mixing up to the mixing ratio of 50/50 for Pt–Co(mqph)/C and 80/20 for Pt–Ni(mqph)/C, respectively. However, larger amounts of M(mqph) caused a decrease in the catalytic activities. The similar trends are also observed in the initiation potential E_{ini} defined as the potential at $I = 1 \text{ mA mg}_{\text{Pt}}^{-1}$, and the current maximum value I_{max} for the MOR (Fig. 4(a) and (b)). Co(mqph)/C and Ni(mqph)/C catalysts themselves showed no catalytic activity for the MOR. These facts suggest that these organic metal complexes play a role in promoting the electrochemical MOR that is occurring on the Pt catalyst.

3.2. Structural and chemical states analyses of heat-treated Pt–M(complex)/C mixed catalysts

In order to clarify the mechanisms of the electrochemical MOR on the Pt–M(complex)/C mixed catalysts and to identify the electro-catalytic effect for various ligand structures of the organic metal complexes, the spectroscopic characterization was

conducted for various pairs of mixed catalysts before and after the heat-treatment.

Fig. 5 illustrates the XPS spectra of Pt $4f_{5/2}$ (left) and $4f_{7/2}$ (right), Co $2p_{1/2}$ (left) and $2p_{3/2}$ (right), and Ni $2p_{1/2}$ (left) and $2p_{3/2}$ (right) for Pt–M(complex)/C mixed catalysts with the mixing ratio of 50/50 before and after the heat-treatment at 600°C in Ar atmosphere. For all the mixed catalysts, Pt $4f_{5/2}$ and $4f_{7/2}$ peaks shifted to lower energy values after the heat-treatment, and the peak position was near to 71.2 eV for Pt metal. This indicates that most Pt(NH₃)₄Cl₂·*x*H₂O loaded on graphite powder became Pt metal and/or Pt–M (Co or Ni) alloys through the heat-treatment [17]. On the other hand, the peak shifts were small for the Co $2p_{1/2}$ and $2p_{3/2}$ peaks in Pt–Co(complex)/C and for the Ni $2p_{1/2}$ and $2p_{3/2}$ peaks in Pt–Ni(complex)/C through the heat-treatment, and new shoulder peaks appeared at smaller energy positions 778.3 and 852.7 eV corresponding to Co and Ni metals, respectively. Therefore, it can be concluded that although the precursors of the co-catalysts loaded on graphite powder are partially decomposed by the heat-treatment, the central metal coordination structures of the organic metal complexes would remain more or less intact on the graphite powder.

Fig. 6 is the pseudo-radial structure function (RSF) around Co ion for the Pt–Co(complex)/C mixed catalysts obtained from Co K-edge extended X-ray absorption fine structure (EXAFS) spectra before and after the heat-treatment together with those of Co metal and [Co(NH₃)₆]Cl₃ as reference compounds. For the Co(mqph), the first peak appeared at around 1.4 Å corre-

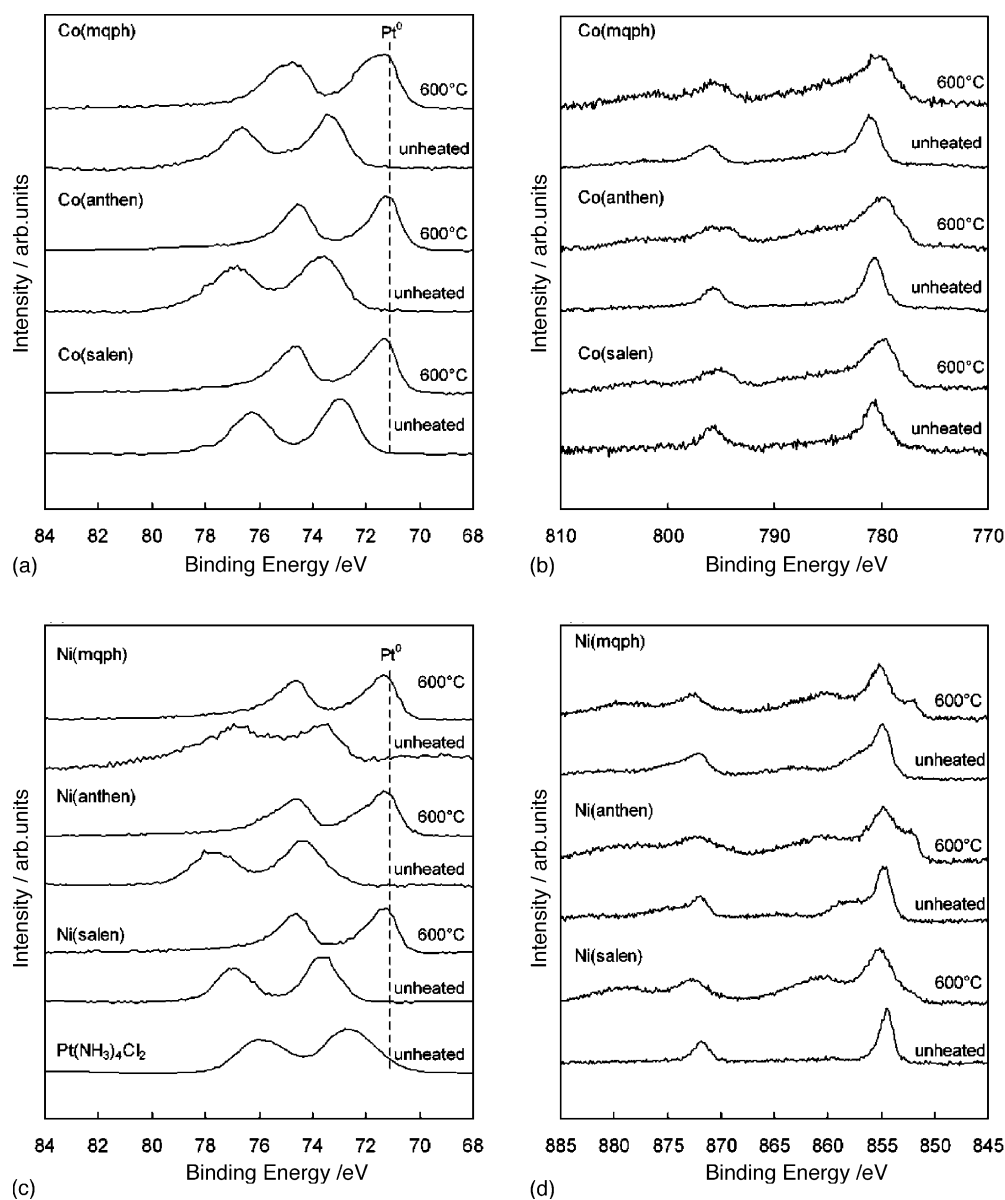


Fig. 5. XPS spectra for the Pt–M(complex)/C mixed catalysts (mixing ratio = 50/50). (a) and (c): Pt $4f_{5/2}$ and $4f_{7/2}$, (b): Co $2p_{1/2}$ and $2p_{3/2}$, (d): Ni $2p_{1/2}$ and $2p_{3/2}$.

sponding to the Co–N interaction (referred by the first peak of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$) and this peak slightly shifted to a larger distance through the heat-treatment. For the Co(anthen) and Co(salen), the peaks became smaller and a novel peak at 2.2 \AA corresponding to Co metal appeared, indicating a partial demetallation of the complexes. These results indicate that the Co– N_3 coordination structure in Co(mqph) would remain after the heat-treatment to a larger extent than the Co– N_4 and Co– N_2O_2 coordination structures in Co(anthen) and Co(salen). van Veen et al. [21] also prepared several Co– N_4 catalysts on carbon black (Vulcan XC-72R) in a similar way. They used various nitrogen ligands and examined their catalytic activities for the electrochemical reduction of oxygen. They also applied EXAFS measurement to check whether the Co– N_4 moieties were remained after the heat-treatment at 700°C and confirmed that the Co– N_4 moieties exist on the carbon black, although some metallic cobalt also appeared.

Fig. 7 shows the Co K-edge X-ray absorption near-edge structure (XANES) spectra of Co ion for the Pt–Co(complex)/C mixed catalysts before and after the heat-treatment. All the Co K-edge XANES spectra are located between the spectra for Co metal and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. For the Co(anthen) and Co(salen), the XANES spectra shifted to lower energy direction through the heat-treatment than that for the Co(mqph). These facts mean that the metal coordination structures of the organic metal complexes were partially decomposed through the heat-treatment to form Co metal, and for Co(anthen) and Co(salen) the decomposition progressed more quickly than for Co(mqph). However, the major trend was that the metal coordination structures in the Co(complex) more or less remained on the graphite powder even after such a severe heat-treatment.

The above results of XPS and XAFS measurements are in good agreements with our previous data [17] by thermogravimetry and differential thermal analysis (TG-DTA), trans-

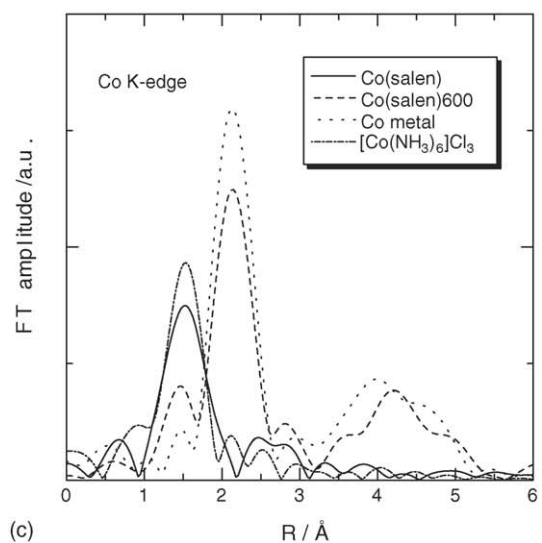
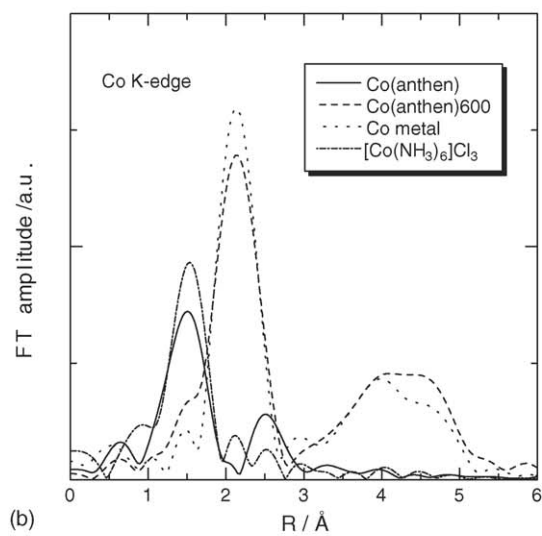
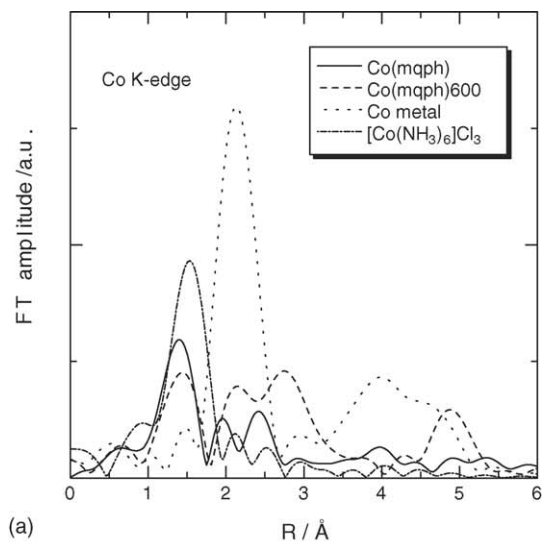


Fig. 6. RSFs for the Pt–Co(complex)/C mixed catalysts (mixing ratio: 50/50) around Co ion obtained by Co K-edge EXAFS spectra. (a) Co(mqph), (b) Co(anthen) and (c) Co(salen).

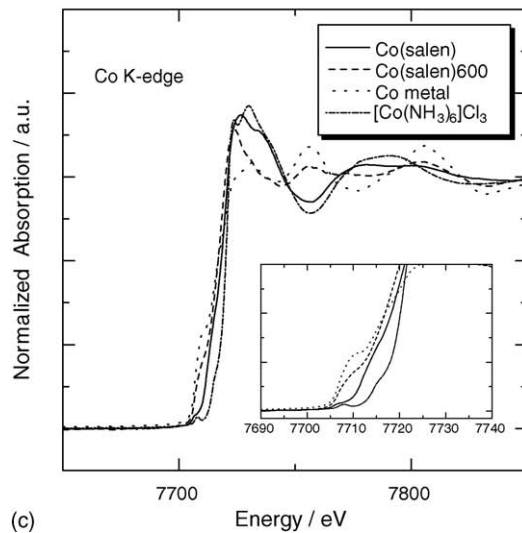
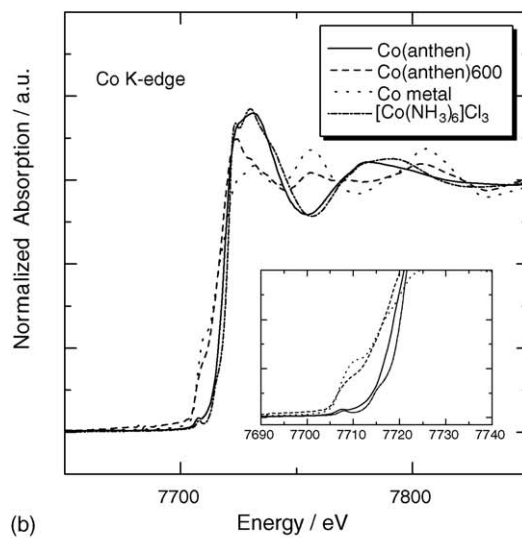
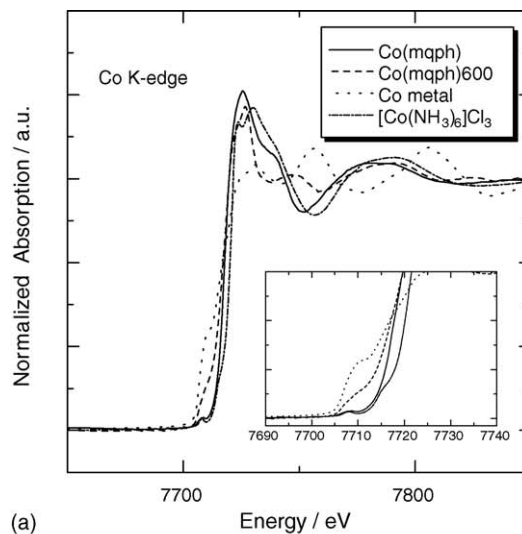


Fig. 7. Co K-edge XANES spectra for the Pt–Co(complex)/C mixed catalysts (mixing ratio: 50/50). (a) Co(mqph), (b) Co(anthen) and (c) Co(salen).

mission electron microscope (TEM) morphologies, EDX elemental analysis and X-ray diffraction (XRD) patterns. From those results, the precursor of Pt, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$, was completely decomposed by the heat-treatment up to 400°C , while M(mqph), M(anthen) and M(salen), especially in the mixed state, exhibited more mild decompositions than the $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$ and even at 600°C no complete decompositions were observed. TEM and EDX indicated that the alloy formation is not directly connected to the MOR activity. Therefore, it is anticipated that the metal coordination structures in the M(complex)s that remained on the graphite powder play a role in promoting the effective MOR on the Pt catalysts.

3.3. Interaction of organic metal complexes with adsorbed species

As mentioned in the above sections, the metal complex in Pt–M(complex)/C mixed catalysts would partially be decomposed by the heat-treatment, but the central metal coordination structures tend to remain on the graphite powder. Therefore, the possible mechanisms of MOR on Pt–M(complex)/C mixed catalysts could be assumed as in the following: (i) the M(complex)s play a similar role as Ru in the Pt–Ru alloy catalyst, i.e. the MN_xO_y structures in M(complex) dissociate H_2O to form M–OH and make CO on Pt oxidize (Eqs. (3)–(5)), and/or (ii)

the MN_xO_y structures directly interact with CO more strongly than Pt and make CO oxidize on themselves. Here, the nickel complexes, Ni(complex) of various molecular forms are used as the model compounds and their interaction energy with OH^- or CO is estimated using ab initio calculation, to investigate the correlation between the interaction energy and the enhancement of electrochemical MOR on Pt–Ni(complex)/C mixed catalysts.

Fig. 8 shows the optimized geometries of the organic metal complexes at the HF/6-31G* level.

Fig. 9 shows the optimized structures of organic metal complexes interacting with OH^- and CO. The optimized structures indicate that all the organic metal complexes interact with OH^- and CO on the Ni metal site. For Ni(anthen) and Ni(salen), OH^- or CO coordinates to the Ni site from the direction perpendicular to the aromatic rings while for Ni(mqph), these tend to be coordinated from the ligand-free direction of the Ni–N₃ site. The calculated interaction energies (ΔE_{int}) of the organic metal complexes with OH^- and CO are shown in Fig. 10. The ΔE_{int} values for the OH^- complexes are found to be larger (more negative) than those of the CO complexes. Especially the ΔE_{int} value for OH^- complex of Ni(mqph) is quite larger than those of the other complexes. The calculated large interaction energy of the Ni(mqph) complex with OH^- shows the existence of strong interaction between Ni and OH^- in this complex.

Fig. 11 shows the LUMOs of the Ni complexes calculated at the HF/6-31G* level. The LUMO of Ni(mqph) localizes

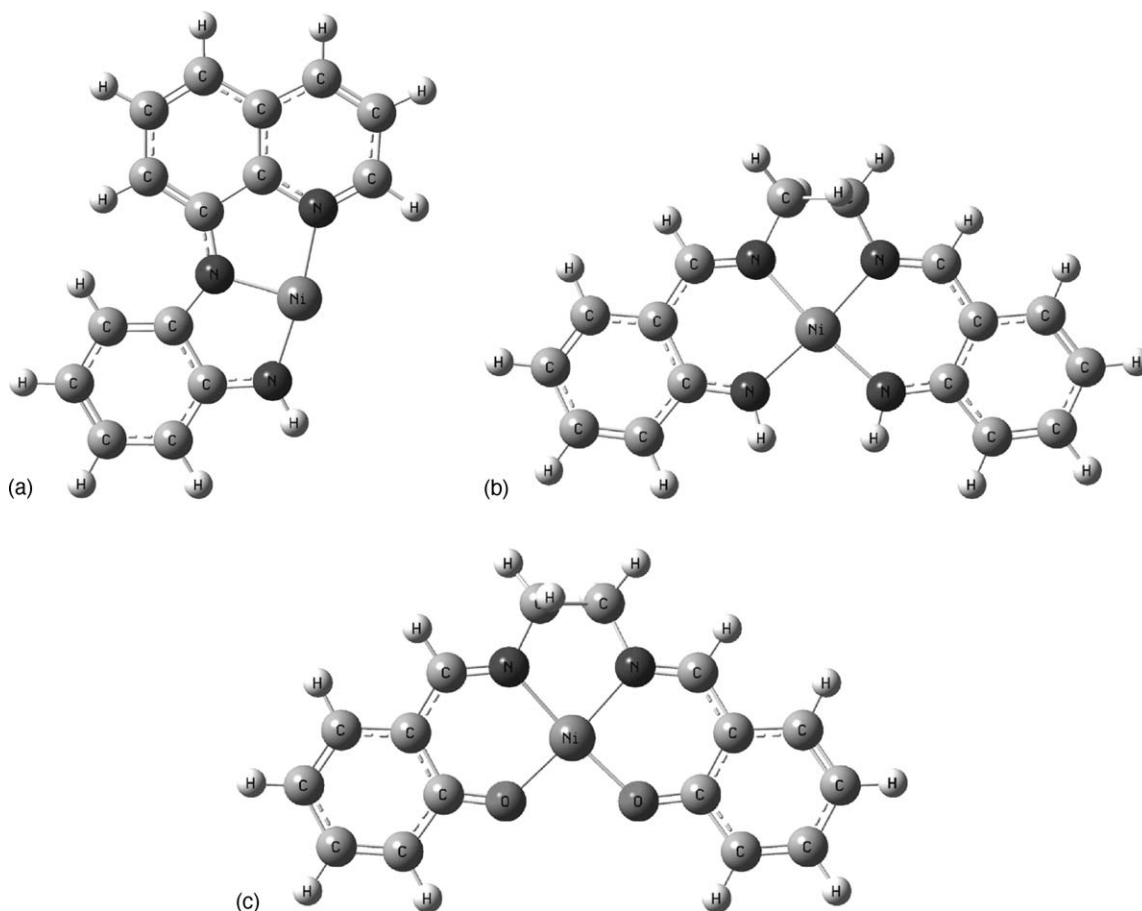


Fig. 8. Optimized geometries of the organic metal complexes. (a) Ni(mqph), (b) Ni(anthen) and (c) Ni(salen). HF/6-31G*/HF/6-31G*.

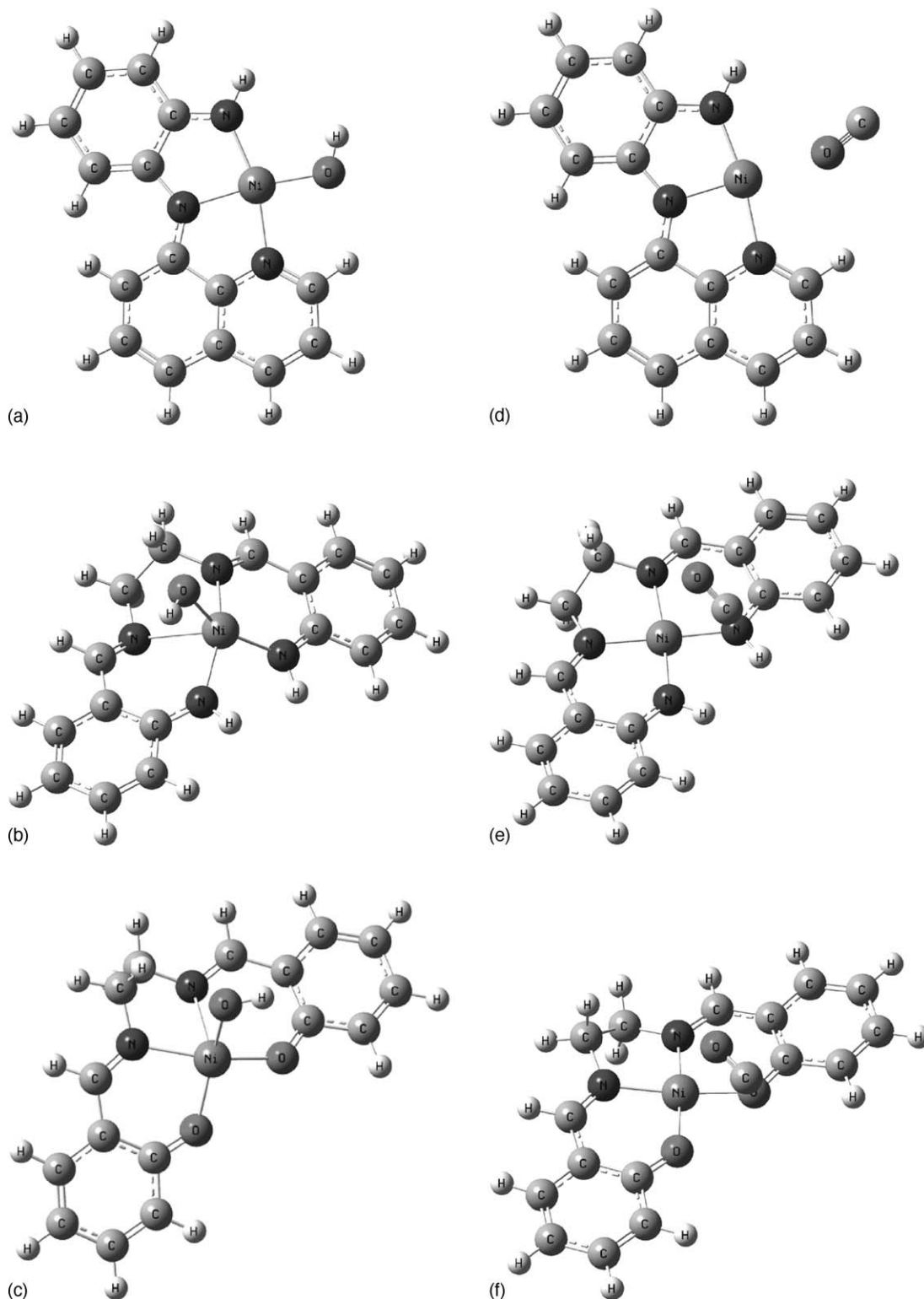


Fig. 9. Optimized geometries of the organic metal complexes interacting with OH⁻ and CO species. OH⁻: (a) Ni(mqph), (b) Ni(anthen) and (c) Ni(salen). CO: (d) Ni(mqph), (e) Ni(anthen) and (f) Ni(salen). HF/6-31G**/HF/6-31G**.

on the Ni metal site, while the LUMOs for Ni(anthen) and Ni(salen) delocalize to the aromatic rings. The OH⁻ interacts with Ni(mqph) from the direction where the LUMO of Ni(mqph) extends outside. The geometry of the complex suggests that

orbital–orbital interaction is a cause of the strong attraction between the OH⁻ and Ni(mqph) [22]. The stronger MOR activity of the Ni(mqph) complex compared with other complexes can be explained by the larger interaction energy of the complex

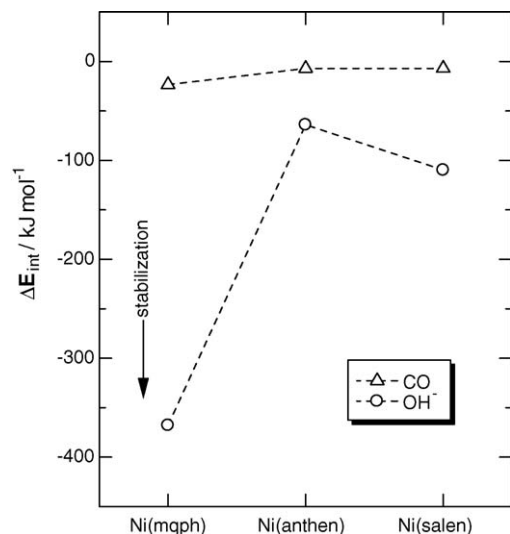


Fig. 10. Interaction energies ΔE_{int} of the organic metal complexes with OH⁻ or CO. MP2/6-311+G**//HF/6-31G*.

with OH⁻. The larger binding energy stabilizes the OH⁻ species on the surface, which would enhance the oxidation of CO on metal surface.

4. Conclusions

The electrochemical MOR behaviors on Pt–M(complex)/C mixed catalysts in acidic media were examined to investigate the mixing effect of organic metal complex to Pt/C catalyst. All the co-catalysts resulted in higher catalytic activities for the electrochemical MOR than Pt/C catalyst and especially Pt–Ni(mqph)/C and Pt–Co(mqph)/C enhanced efficiently the MOR. The catalytic enhancement of the M(mqph)s increased up to the mixing ratio of 50/50 for Pt–Co(mqph) and 80/20 for Pt–Ni(mqph) pairs, respectively. However, larger amounts of M(mqph)s caused a decrease in catalytic activity, which indicates that M(complex) shows no catalytic activity but works as a co-catalyst with Pt. It is suggested that the organic metal complexes, especially M(mqph), promote the electrochemical MOR on Pt as a promoter and the mixing effect for the MOR depends on the central

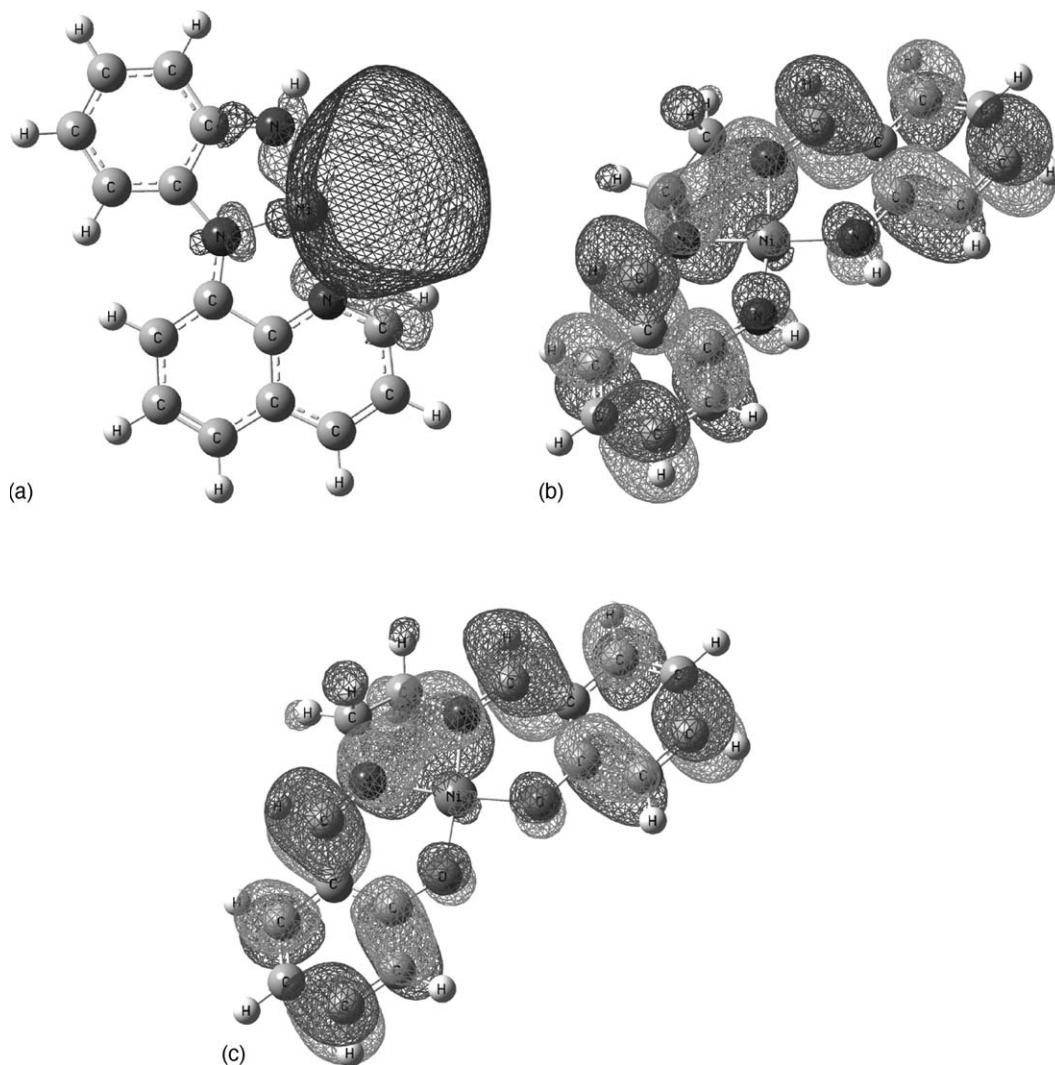


Fig. 11. LUMOs in the organic metal complexes. (a) Ni(mqph), (b) Ni(anthen) and (c) Ni(salen). HF/6-31G**//HF/6-31G*.

metal and the ligand structure of organic metal complexes. XPS and XAS measurements for the Pt–M(complex)/C mixed catalysts showed that the MN_xO_y structures of M(complex) were retained on the graphite powder although some portions were decomposed by the severe heat-treatment conditions at 600 °C in Ar atmosphere. Ab initio calculations for the Ni(complex)s exhibited that the Ni metal site in Ni(mqph) interacts with OH^- more strongly than those of the other organic metal complexes, which agrees well with the results of the electrochemical MOR in the acidic media. This fact suggests that the Pt–M(mqph)/C electro-oxidizes a byproduct CO adsorbed on Pt by “bifunctional effect” similarly to Pt–Ru alloy catalysts, which promote the effective electrochemical MOR.

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