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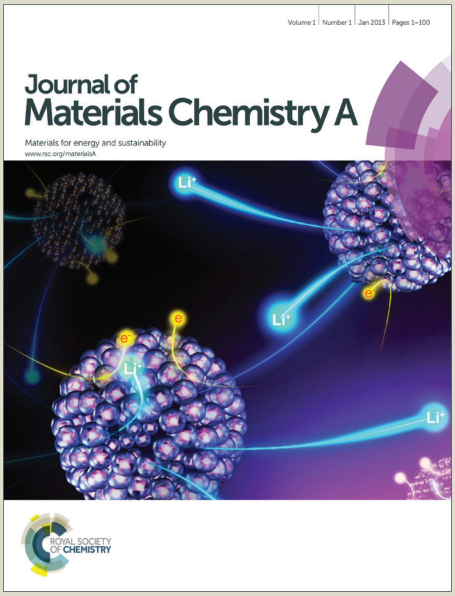

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ARTICLE TYPE

Dual-dehydrogenation-promoted catalytic oxidation of formaldehyde on alkali-treated Pt clusters at room temperature

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The activity of Pt catalyst toward room-temperature catalytic oxidation of formaldehyde (HCHO) known as a common indoor air pollutant can be remarkably improved by addition of some alkali metal salts. The resulting enhancement in catalytic activity of Pt catalyst is generally attributed to the introduction of alkali metal ions. Presented here, theoretical simulations and experimental studies show that the OH^- ions provided by alkali metal salts make a major contribution to the enhanced activity of Pt catalysts toward the room-temperature catalytic oxidation of HCHO instead of additional alkali metal ions. This is because Cl^- ions from Pt precursor (H_2PtCl_6) are easily chemisorbed on prepared Pt catalysts, leading to their deactivation. The OH^- ions provided by some alkali metal salts can effectively substitute surface adsorbed Cl^- ions and contribute to the dual dehydrogenation of HCHO molecule, which promotes the regeneration of Pt catalysts and activation of O_2 molecule. Those findings are significant for optimizing the surface structure of Pt catalysts and further preparing the high-performance Pt catalysts for room-temperature catalytic oxidation of HCHO.

1. Introduction

The noble metal platinum (Pt) is a common catalyst for removing the poisonous formaldehyde (HCHO) gas from indoor air by the room-temperature catalytic oxidation.[1-4] Unfortunately, the high price of Pt catalyst increases the cost of indoor HCHO elimination. Improving the mass activity of Pt is considered as one of the most promising methods for minimizing the required amount of this catalyst. It is generally believed that the reduction of the Pt cluster size can increase the number of reaction sites.[5-7] Thus, the high mass activity of Pt for the catalytic oxidation of HCHO can be achieved by reducing the size of Pt clusters to the nanoscale range.[8] However, it is argued that a decrease in the size of Pt clusters unavoidably increases the number of seriously unsaturated edge Pt atoms, which easily bonds with some O-containing species.[9,10] Consequently, the catalytic activity of these nanosized Pt clusters is still limited. Besides, the nanosized Pt clusters with high surface energy require to be stabilized by adsorption of some foreign ions, which lead to the change in their surface structure. Therefore, it is guessed that the adsorbed species/ions during preparation process probably influence the catalytic activity of the resulting Pt clusters.

Previous reports on the addition of alkali metal (Na and K) ions into the catalyst show a dramatic improvement of mass activity of Pt toward room-temperature catalytic oxidation of HCHO.[8,11] It seems that this phenomenon can also occur in the other catalytic systems (Ag and Pd).[12.13] However, the effect of anions from alkali metal salt solution on the catalytic activity of Pt clusters is rarely discussed.[14] Our recent works suggest that the surface OH^- species from NaOH solution can enhance the catalytic activity of Pt clusters for the room-temperature catalytic oxidation of HCHO.[15,16] Despite those efforts, the effect of alkali metal salt addition on the activity of Pt clusters toward room-temperature catalytic oxidation of HCHO is not yet completely understood. A clear understanding of the mechanism of room-temperature catalytic oxidation of HCHO on Pt clusters is also missing. As a result, no convincing strategy has been so far outlined how to use the full potential of Pt catalysts for the room-temperature catalytic oxidation of HCHO.

Herein, we present theoretical simulations and experimental studies to investigate the effect of alkali metal salt addition on the activity of Pt catalysts toward room-temperature catalytic oxidation of HCHO. A novel dual-dehydrogenation-promoted room-temperature catalytic oxidation mechanism for HCHO on Pt clusters is proposed. According to this mechanism, substituting inactive Cl^- ions adsorbed on Pt clusters by active OH^- ions from alkali metal salt solution is considered to be response for the enhanced activity of Pt catalyst toward room-temperature catalytic oxidation of HCHO. We believe that this study can guide the synthesis and optimization of Pt catalysts for room-temperature catalytic oxidation reactions.

2. Experimental and theoretical section

2.1 Materials synthesis.

P25 titania is used as the carrier of Pt catalyst. Catalysts are synthesized by reducing H_2PtCl_6 with $NaBH_4$ on P25 surface. Sample I was synthesized by impregnation of P25 with Pt precursor (H_2PtCl_6) followed by reduction with $NaBH_4$. Sample II and sample III were prepared by washing sample I with NaOH and Na_2CO_3 aqueous solutions, respectively. The synthesis of sample IV was similar to that of sample I except NaOH addition in $NaBH_4$ aqueous solution. Sample V was obtained by washing Sample IV with NaCl aqueous solution and Sample VI by washing Sample V with NaOH aqueous solution. Experimental details are provided in Supporting Information.

2.2 Catalyst characterization.

High-resolution transmission electron microscopy (HRTEM) analysis was conducted on a Titan G^2 60-300 Probe Cs Corrector HRSTEM with a 300 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi electron spectrometer with Mg Kα (1253.6 eV) source. All binding energies were referenced to the C 1s peaks at 284.8 eV from the adventitious carbon.

2.3 Catalytic activity measurements.

The catalytic activities of samples I, II, III, IV, V and VI toward HCHO oxidation were measured in a dark organic glass box equipped with a 5 W fan at room temperature (25 °C) in the similar way reported in our previous works.[15,16] 0.1 g of each sample was dispersed on the bottom of a Petri glass dish with the diameter of 14 cm. After that, the dish was covered by a piece of glass slide and then placed in the bottom of the reactor. 10 μL of condensed HCHO (38%) was injected into the reactor. The concentration of gaseous HCHO was on-line analyzed by a Photoacoustic IR Multigas Monitor (INNOVA air Tech Instruments Model 1412). The initial equilibrium concentration of HCHO was controlled at about 235 ppm. After that, the glass slide on the simple-coated dish was removed to start the catalytic oxidation of HCHO. The decreased concentration of HCHO was used to evaluate the catalytic activity of sample.

2.4 Theoretical simulation.

The room-temperature catalytic oxidation of HCHO on Pt catalysts was investigated by the density functional theory (DFT) calculations based on the CASTEP package.[17] A Pt_{43} cluster with diameter of 1 nm is used as the catalyst model, which consists of 43 Pt atoms (Fig. S1). Considering the spontaneity of room-temperature catalytic oxidation of HCHO, a simulation strategy was created on the basis of the chemical adsorption of reactant molecules and physical desorption of the product molecules on/from Pt clusters. In the initial stage of catalytic reaction, the reactant molecule is activated by its chemisorption on Pt catalyst, which can weaken some of its chemical bonds. These weakened chemical bonds are the potential reaction centers because they can be easily broken under influence of other reactant molecules. Meanwhile, the product molecules are generated with new chemical bonds. Different from the reactant molecules, the product molecules should exist on the Pt catalyst surface in the form of physical adsorbed species. Thus, the product molecule can be easily desorbed from Pt catalyst via the natural thermal motion. The above total catalytic process effectively avoids the large energy barrier, which is a common feature of the room-temperature catalytic oxidation of HCHO. The adsorption energy (E_{ads}) of reactant molecules and the desorption energy (E_{des}) of product molecules on Pt clusters are calculated as follows:

$$E_{\text{ads}} = E_{\text{catalyst}} + E_{\text{reactant}} - E_{\text{total}} \quad (1)$$

$$E_{\text{des}} = E_{\text{total}} - E_{\text{catalyst}} - E_{\text{product}} \quad (2)$$

where E_{catalyst} stands for the free energy of Pt catalyst, E_{reactant} is the free energy of a reactant molecule (Fig. S2), E_{total} is the total free energy of the molecule-adsorbed Pt catalyst and E_{product} is the free energy of the product molecule.

3. Results and discussion

3.1 Surface modification and catalytic activity of Pt catalysts.

The XPS analysis shows that an obvious peak of Cl 2p appears in sample I obtained from the reduction of H_2PtCl_6 in $NaBH_4$ aqueous solution (Fig. 1a). Catalytic activity test indicates that sample I nearly does not show activity for the catalytic oxidation of HCHO (Fig. 1b and Fig. S3) though Na^+ ions from $NaBH_4$ are introduced onto the catalyst (Fig. S4c) and H_2PtCl_6 is well reduced (Fig. S4d). However, the peak of Cl 2p for sample IV synthesized in the mixed solution of $NaBH_4$ and NaOH is extremely weak and sample IV shows high activity toward catalytic oxidation of HCHO. It should be noted that the adsorption of Cl^- ion on P25 is weak, even on the high-energy anatase TiO_2 {001} surface.[18] Here the calculated results confirm that Cl^- and Na^+ ions can be chemisorbed on Pt cluster (Fig. 1c). Hence, it is speculated that the detected Cl species are mainly originated from the surface adsorbed Cl^- ions on Pt clusters. Furthermore, some reports suggest that NaOH addition can decrease the size of the prepared Pt clusters and improves their catalytic activity because the chemisorption of OH^- and Na^+ ions on Pt clusters can stabilize the nanosized Pt clusters by decreasing their surface energies (Fig. 1d).[8,11] However, in the present preparation, NaOH addition does not influence the size of Pt clusters because the nucleation rate of Pt clusters is larger than the growth rate in the strongly reducing $NaBH_4$ aqueous solution (Fig. S5). Thus sample I and sample IV share similar cluster size distribution from 2 nm to 3 nm. In addition, the NaOH-washing treatment almost does not change the Pt content of all samples (Table S1). Therefore, the poor activity of sample I is considered from the adsorption of Cl^- ions on Pt catalysts. To further confirm it, sample I was treated with NaOH aqueous solution. The peak of Cl 2p for the resulting sample II becomes negligible. Besides, sample II shows nearly the same activity for the catalytic oxidation of HCHO as sample IV. This can be explained because the adsorption energy (E_{ads} = 4.49 eV) of Cl^- and Na^+ ions on Pt cluster is smaller than that (5.70 eV) of OH^- and Na^+ ions (Fig. 1d). Thus the adsorbed Cl^- ions on Pt catalysts are easily substituted by OH^- ions.

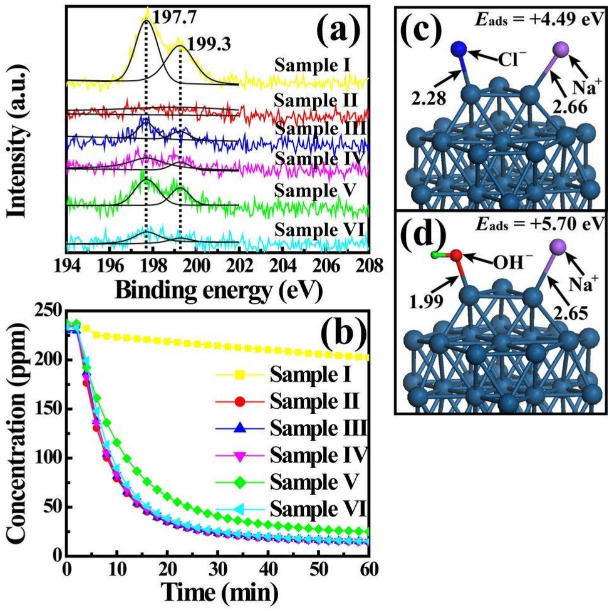

Fig. 1 Effect of surface modification of Pt catalysts on their catalytic activities: (a) High-resolution XPS spectra of Cl 2p regions for samples I, II, III, IV, V and VI, (b) formaldehyde concentration as a function of the reaction time and (c-d) adsorption of Na^+, Cl^- and OH^- ions on Pt clusters. High-resolution XPS spectra of other elements are shown in Fig. S4.

In the previous literatures, Na_2CO_3 is often used in the preparation of highly-active Pt catalysts. Similarly, sample III obtained by Na_2CO_3-washing treatment of sample I also shows the same high catalytic activity as sample IV and the peak of Cl 2p for sample III also becomes weak. This is not surprising because Na_2CO_3 is also a strong alkali like NaOH, which can produce a large number of OH^- ions by the hydrolysis of CO_3^{2-} ions. In contrast, sample IV is treated by NaCl aqueous solution. The resulting sample V shows a small decrease in the activity. The XPS analysis suggests that the peak of Cl 2p in sample V is slightly enhanced as compared to that in sample IV, indicating that a small number of Cl^- ions are introduced onto Pt clusters. This also implies that Cl^- ions are difficult to substitute the OH^- ions adsorbed on Pt catalysts. However, Cl^- ions adsorbed on Pt catalysts can be easily eliminated by OH^- ions. This is consistent with the previous analysis. Thus, sample VI obtained from NaOH-washing treatment of sample V exhibits the same catalytic activity as sample IV. According to above experiments, a fact is revealed that the anions from alkali metal salts determine the activity of prepared Pt catalysts toward room-temperature catalytic oxidation of HCHO instead of cations. Substituting adsorbed Cl^- ions by OH^- ions contributes to the enhanced activity of Pt catalysts. However, the difference in the chemical nature of surface Cl^- ions and OH^- ions on Pt catalysts is not understood.

3.2 Room-temperature catalytic oxidation of HCHO

To illustrate the effect of surface Cl^- ions and OH^- ions on the catalytic activity of Pt clusters, the room-temperature catalytic oxidation mechanism of HCHO on Pt cluster is firstly investigated. In comparison to HCHO molecule, O_2 molecule is easier to be chemisorbed on Pt cluster because adsorption energy (E_{ads} = 1.83 eV in Fig. 2b) of a single O_2 molecule on the Pt cluster doubles that (0.89 eV in Fig. S6) of a single HCHO molecule. Furthermore, the adsorptions of O_2 molecules {101}, {100} and {001} surfaces of TiO_2 are also weak, which cannot lead to the activation of O_2 molecule (Fig. S7). Thus, adsorption of O_2 molecules on Pt clusters is dominant. In the formed surface O_2 species, the two-coordination O (O_{2C}) atom with higher saturation possesses relatively weaker bonding ability than the one-coordination O (O_{1C}) atom. In HCHO molecule, the C=O bond is more stable than the C–H bond. Thus, the C–H bond may be preferentially broken during the catalytic oxidation reaction. Hence, it is speculated that the new chemical bond tends to form between the O_{1C} atom of surface O_2 species and the H atom of HCHO molecules. However, this does not occur when the H atom of HCHO is close to the O_{1C} atom (Fig. S8) due to the fact that the strong chemical bond still exists between O_{1C} and O_{2C} atoms though the O–O bond is slightly lengthened after chemisorption of O_2 molecule. Thus, the bonding ability (chemical activity) of O_{1C} atom is limited. Surprisingly, two O–H bonds are formed when two H atoms of HCHO molecule are simultaneously close to the O_{1C} and O_{2C} atoms, respectively (Fig. 2c). As a result, the HCHO molecule is oxidized to one CO molecule physically adsorbed on Pt cluster, while the surface O_2 species is reduced to one H_2O_2-like (−OHOH) group chemically adsorbed on Pt cluster.[19] This can be explained because the synchronous formation of two O–H bonds can greatly weaken the chemical bond between the two O atoms in the surface O_2 species. Thus, the O–O bond is lengthened to 1.71 Å and the outer hydroxyl (–OH) group in –OHOH group is approximate to a free hydroxyl (•OH) radical known as a highly-active oxidizing species.[20] Hence, it is concluded that the dual dehydrogenation of HCHO molecule can effectively activate the surface O_2 species on Pt cluster. After CO molecule is physically desorbed from Pt cluster (Fig. 2d), the –OHOH group with high oxidizing activity can directly deprive HCHO molecule of one H atom (Fig. 2e).[20,21] As a result, the HCHO molecule is oxidized into one free aldehyde (•CHO) radical, and the –OHOH group is reduced into one H_2O molecule and one –OH group. Different from the outer –OH in –OHOH group, the –OH group left on Pt cluster cannot dehydrogenate HCHO molecule (Fig. S9) because the strong Pt–O bond between –OH group and Pt cluster limits the oxidizing activity of –OH group. Besides, the present –OH group also cannot oxidize the formed CO molecule (Fig. S10). However, as the oxidized intermediate of HCHO molecule, the •CHO radical is highly-active reducing species due to its relatively longer C–H bond and unstable asymmetric structure. Consequently, the –OH group shows the oxidizing activity toward •CHO radical (Fig. 2g). The –OH group and •CHO radical are converted to one H_2O molecule and one CO molecule, respectively. The formed H_2O and CO molecules both can be physically desorbed from Pt cluster. After that, the Pt cluster recovers to its initial chemical state (Fig. 2a). The above presented dehydrogenation oxidation of HCHO molecule on Pt cluster can be summarized by the following chemical equation:

$$2HCHO + O_2 + Pt \rightarrow 2CO + 2H_2O + Pt \qquad (3)$$

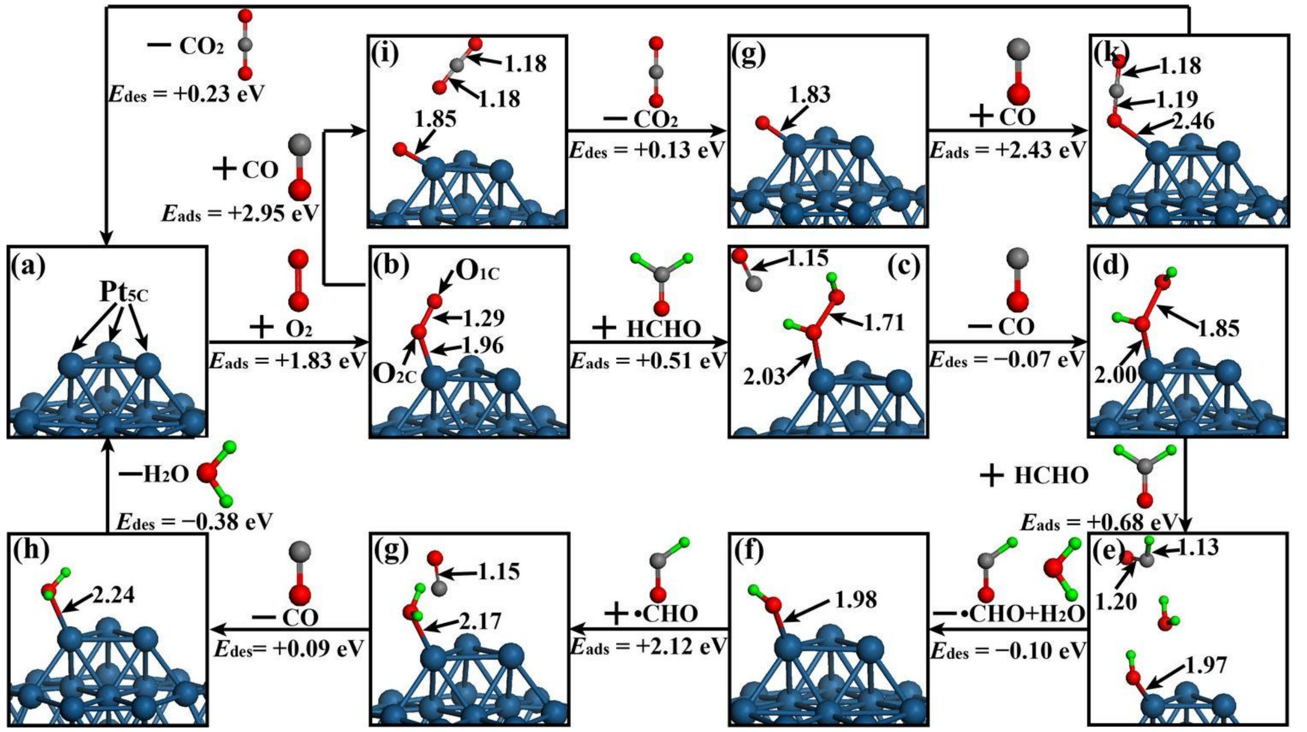

Fig. 2 Catalytic oxidation of HCHO molecule on Pt cluster. The numbers pointing to atoms stand for the lengths (Å) of bonds. The plus (+) and minus (–) signs represent the adsorption of reactant molecule and desorption of product molecule, respectively. The steel-blue sphere stands for Pt atoms, the red one for O atoms, the grey one for C atoms and the green one for H atoms.

As for the two remaining CO molecules, Pt cluster can use one newly adsorbed O_2 molecule to directly oxidize them into two CO_2 molecules by two steps. Firstly, the O_{1C} atom in surface O_2 species bonds with the C atom of CO molecule (Fig. 2i). Then the O–O bond in surface O_2 species is broken and one CO_2 molecule is formed. After CO_2 molecule is desorbed from Pt cluster, one –O group is left on Pt cluster (Fig. 2g). Like the –OH group in Fig. 2f, the present –O group also possesses a low oxidizing ability due to the limitation originating from the Pt–O bond, which cannot dehydrogenate HCHO molecule (Fig. S11). However, the –O group can oxidize CO molecule by forming one stable C–O bond (Fig. 2k). Due to the formation C–O bond, the Pt–O bond is weakened and the formed CO_2 molecule can be desorbed from Pt cluster. The corresponding chemical equation of CO oxidation is as follows:

$$2CO + O_2 + Pt \rightarrow 2CO_2 + Pt \qquad (4)$$

Furthermore, thermodynamic data indicates that the oxidation of CO molecule on Pt cluster occurs prior to the dehydrogenation of HCHO molecule due to the obviously higher E_{ads} (2.95 and 2.43 eV) of CO molecule on surface O_2 species as compared to that of HCHO molecule. This implies that the dehydrogenation of HCHO molecule probably determines the rate of HCHO oxidation.

3.3 Dual dehydrogenation of HCHO with two adjacent –OH groups

The above simulation well describes the catalytic oxidation of HCHO on Pt cluster. However, in the case of real catalytic reactions, some intermediate products can be physically desorbed from one Pt cluster (or atom) and then transferred to another Pt cluster (or atom). Besides, due to the randomness of adsorption and desorption molecular processes, the catalytic reactions occurring on all Pt clusters cannot be in the same stage at a given time. Based on these considerations, it is speculated that some side reactions can probably occur. According to thermodynamics, the ·CHO radical with high reducing activity prefers to react with the –OHOH group on Pt cluster (equation (5), Fig. 3) rather than with the –OH group. This is because E_{ads} (4.07 eV) of ·CHO radical on –OHOH group is about twice higher than that on –OH group (2.12 eV in Fig. 2f and 2g). Moreover, E_{ads} (2.88 eV in Fig. 4) of ·CHO radical on –O group (equation (6)) is also larger than that on –OH group. Furthermore, besides HCHO molecule and ·CHO radical, the –OHOH group with high oxidizing activity can also react with CO molecule by forming a stable C–O bond (equation (7), Fig. 5). Similarly, E_{ads} (1.10 eV) of CO molecule on –OHOH group is also larger than that (0.68 eV in Fig. 2d and 2e) of HCHO molecule on –OHOH group. The formed ·COOH radical can continue to react with another –OHOH group on Pt cluster (equation (8), Fig. 6). The calculated E_{ads} (5.03 eV) of ·COOH radical on –OHOH group is far larger than those of CO and HCHO molecules on –OHOH group. According to thermodynamics, the above four side reactions are prior to some reactions described in Fig. 2.

$$\cdot CHO + –OHOH + Pt \rightarrow CO + H_2O + –OH + Pt \qquad (5)$$

$$\cdot CHO + –O + Pt \rightarrow CO + –OH + Pt \qquad (6)$$

$$CO + –OHOH + Pt \rightarrow \cdot COOH + –OH + Pt \qquad (7)$$

$$\cdot COOH + –OHOH + Pt \rightarrow H_2CO_3 + –OH + Pt \qquad (8)$$

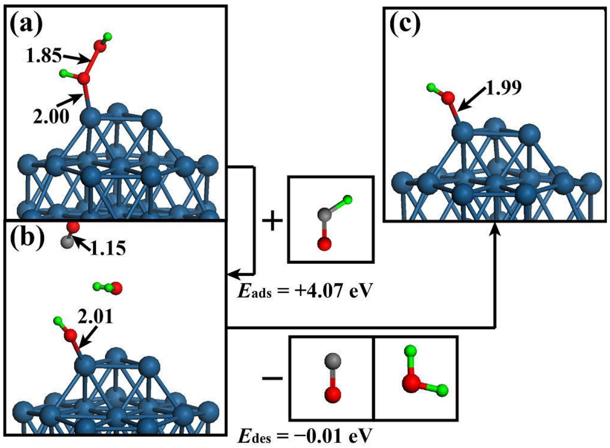

Fig. 3 Reaction between ·CHO group and –OHOH group on Pt cluster. The –OHOH group with high oxidizing activity easily oxidizes ·CHO group into CO molecule on the thermodynamics.

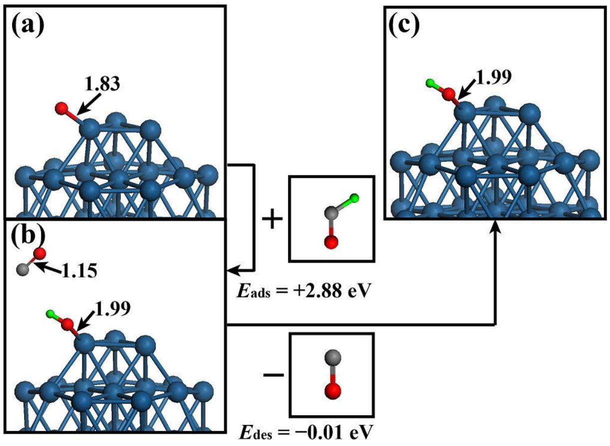

Fig. 4 Reaction between ·CHO group and –O group on Pt cluster. The –O group on Pt cluster dehydrogenates ·CHO group into CO molecule by breaking its C–H bond.

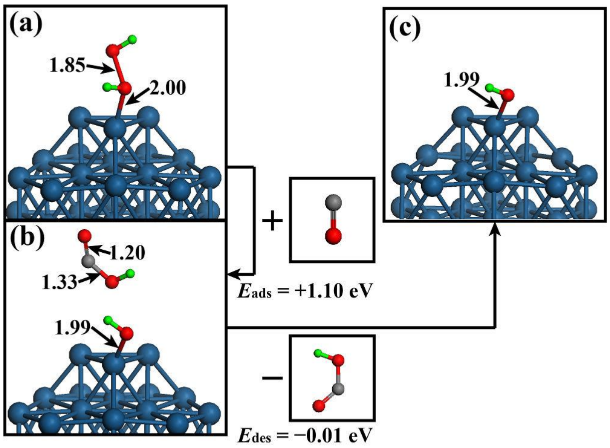

Fig. 5 Reaction between CO molecule and –OHOH group on Pt cluster. The –OHOH group on Pt cluster oxidizes CO molecule into ·COOH radical by forming C–O bond.

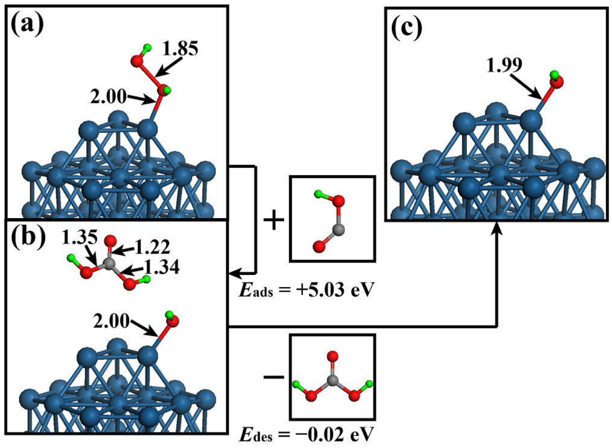

Fig. 6 Reaction between ·COOH radical and –OHOH group on Pt cluster. The –OHOH group on Pt cluster oxidizes ·COOH radical into H_2CO_3 molecule by forming C–O bond.

It should be noted that the above four side reactions share the same feature that one –OH group is left on Pt cluster after reaction. According to the preceding results, the less-active –OH group on Pt cluster can be reduced only by the ·CHO radical. However, the present four side reactions produce not only many –OH groups on Pt cluster, but also consume a large number of ·CHO radicals and –OHOH groups serving as the only oxidizing agent for the production of ·CHO radicals. Hence, it can be speculated that the Pt cluster will be gradually covered by the less-active –OH groups due to the shortage of ·CHO radicals with increasing reaction time. Finally, the Pt cluster will be deactivated because it cannot further chemisorb O_2 molecule. Though the Pt atom bonding with –OH group cannot chemisorb O_2 molecule, its adjacent Pt atom can serve as a chemisorption site (Fig. 7b). The HCHO molecule can be also dually dehydrogenated by the formed surface O_2 species (Fig. 7c) and the formed –OHOH group can oxidize HCHO molecule into ·CHO radical (Fig. 7e). As a result, two adjacent –OH groups are left on Pt cluster (Fig. 7f). The calculated results indicate that two adjacent –OH groups cannot independently oxidize HCHO molecule due to their small oxidizing activities (Fig. S12). However, the dual dehydrogenation of HCHO molecule occurs again when the two H atoms of HCHO molecule are close to the two O atoms of two adjacent –OH groups, respectively (Fig. 7g). Thus, these two adjacent –OH groups are reduced into two H_2O molecules (Fig. 7h), which can be physically desorbed from Pt cluster. Simultaneously, Pt cluster is regenerated (Fig. 7i). Similar to the –OH group, the surface OH^- species can also cooperate with adjacent –OH groups to dually dehydrogenate HCHO molecule (Fig. 8b). Meanwhile, the surface OH^- species and adjacent –OH groups are eliminated in the form of H_2O molecules (Fig. 8c). However, the surface Cl^- species is inactive to the dual dehydrogenation of HCHO molecules in the presence of adjacent –OH groups (Fig. S13), leading to the deactivation of Pt catalysts. As for the surface Na^+ species, Table S1 suggests that the Na contents in sample I, II, III, IV, V and VI do not show obvious difference. However, sample I is mostly inactive to HCHO oxidation. This implies that the Na content is not a key factor determining the catalytic activity of Pt clusters. Furthermore, the Na contents in sample I, II, III, IV, V and VI are obviously higher than Cl and Pt contents. Most Na^+ ions tend to adsorb on TiO_2 because Na^+ ions can form stable chemical bond with the surface O atoms of TiO_2. Thus the effect of Na^+ ions on the catalytic activity of Pt clusters is limited. Hence, it can be concluded that substituting surface Cl^- species by surface OH^- species can promote the regeneration of Pt clusters due to the dual dehydrogenation of HCHO molecule. Thus it is not surprised that the alkali-treated Pt catalysts possess higher catalytic activity than untreated ones containing surface Cl^- species.

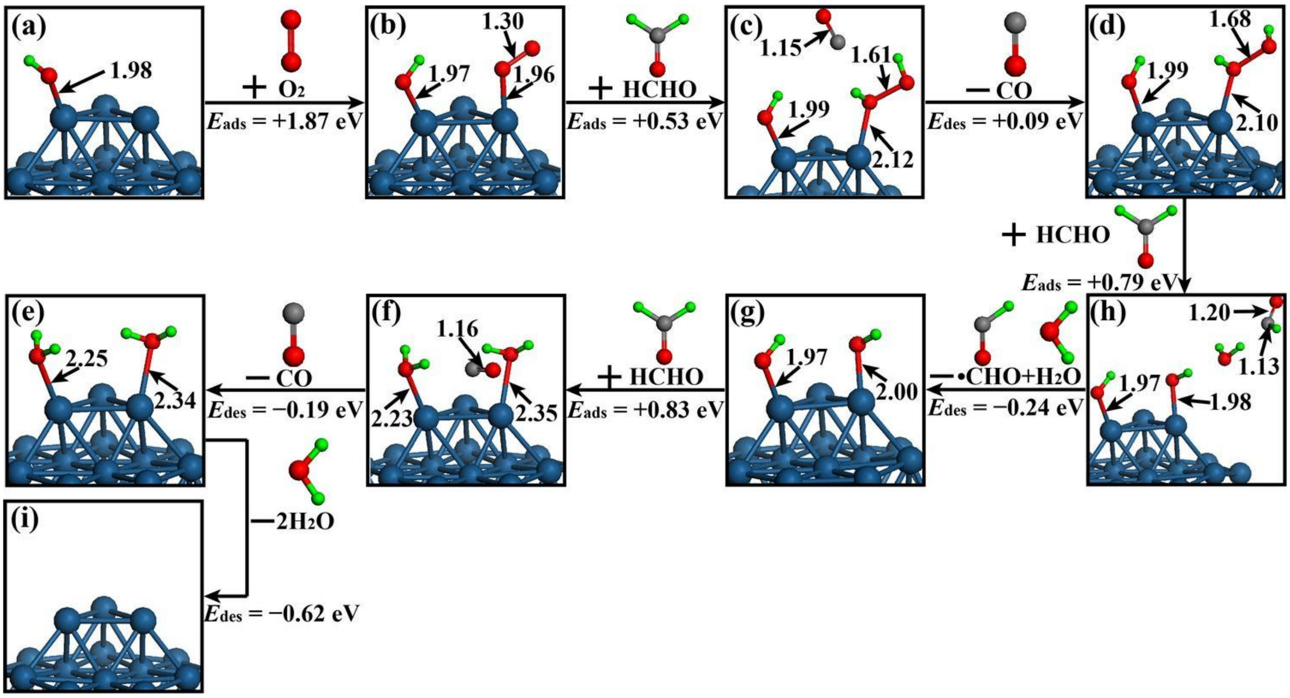

Fig. 7 Dual dehydrogenation of HCHO molecule with two adjacent –OH groups on Pt cluster.

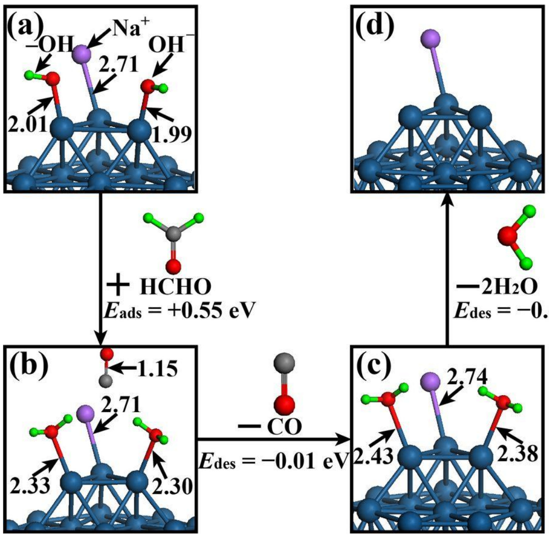

Fig. 8 Dual dehydrogenation of HCHO molecule on NaOH-treated Pt cluster. The blue-violet sphere stands for Na atoms; notation for other atoms as in Fig. 2. The Na^+ ion is used to maintain the charge balance.

4. Conclusion

In summary, theoretical simulations and experimental studies reveal that the OH^- ions provided by alkali metal salts make a considerable contribution to the enhanced activity of Pt catalysts toward the room-temperature catalytic oxidation of HCHO instead of additional alkali metal ions. The nanosized Pt clusters with high surface energy are stabilized by adsorbing OH^-, Cl^- and Na^+ ions. The Cl^- ions from Pt precursor (H_2PtCl_6) are easily chemisorbed on the Pt clusters, leading to the deactivation of Pt catalysts. The alkaline solution treatment can effectively regenerate the Pt clusters by substituting adsorbed Cl^- ions with OH^- ions because the formed surface OH^- species can cooperate with adjacent –OH groups to dually dehydrogenate HCHO molecules. Besides, the dual dehydrogenation of HCHO molecule also determines the activation of O_2 molecule. These results provide a new insight into understanding the effect of alkali metal salt addition on the activity of Pt catalysts for the room-temperature catalytic oxidation of HCHO. The obtained results seem to be very promising for synthesizing high-performance Pt catalysts for the room-temperature catalytic oxidation of HCHO by optimizing the surface structure of Pt clusters.

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TOC Graphics

Dual dehydrogenation of HCHO molecules can promote the activation of O_2 molecules and regeneration of Pt catalysts.