Journal Pre-proof

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PII: S0926-3373(20)30808-0
DOI: <https://doi.org/10.1016/j.apcatb.2020.119393>
Reference: APCATB 119393

To appear in: *Applied Catalysis B: Environmental*

Received Date: 21 May 2020
Revised Date: 31 July 2020
Accepted Date: 3 August 2020

Please cite this article as: Zhou Y-Wei, Chen Y-Feng, Jiang K, Liu Z, Mao Z-Jie, Zhang W-Yi, Lin W-Feng, Cai W-Bin, Probing the Enhanced Methanol Electrooxidation Mechanism on Platinum-Metal Oxide Catalyst, *Applied Catalysis B: Environmental* (2020), doi: <https://doi.org/10.1016/j.apcatb.2020.119393>

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Probing the Enhanced Methanol Electrooxidation Mechanism on Platinum-Metal Oxide Catalyst

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Graphic Abstract

Highlights

- Interface-rich Pt-SnO₂ nanoflakes are developed for methanol oxidation reaction
- Reaction pathway is identified by in situ ATR-SEIRAS and on line DEMS measurements
- Pt-SnO₂ favours the non-CO pathway for MOR due to electronic effect

Abstract

Pt-metal oxide nanocomposites are classified as an alternative promising catalyst besides Pt-Ru nanoalloys for electrochemical methanol oxidation reaction (MOR), and yet the relevant enhancement mechanism for MOR remains largely elusive in terms of catalyst functions and reaction pathways. Herein, interface-rich Pt-SnO₂ nanoflakes supported on reduced graphene oxide have been prepared and employed as a model catalyst for such a study. X-ray photoelectron spectroscopy and X-ray absorption spectroscopy measurements reveal significant electronic structure modification on Pt in contact with SnO₂, concomitant with enhanced MOR. In-situ surface enhanced infrared absorption spectroscopy and on-line differential electrochemical mass spectrometry measurements indicate that the non-CO pathway is selectively enhanced on Pt-SnO₂ compared to the CO pathway which prevails on Pt. DFT calculations reinforce that this electronic structure manipulation favors the non-CO reaction pathway on Pt-SnO₂.

Keywords

Electrocatalytic methanol oxidation; platinum-metal oxide composite catalyst; reaction mechanism identification; spectroelectrochemistry; DFT calculations

1.Introduction

Methanol oxidation reaction (MOR) on Pt-based catalysts is a key reaction in direct methanol fuel cells [1-4] as well as in hybrid methanol electrolyzers for hydrogen production [5, 6]. To date, there are two major challenges facing the Pt-based catalysts, i.e., low abundance and easy deactivation of Pt.[7-9] To develop efficient Pt-based catalysts, it is essential to understand the relevant MOR mechanism. So far, most MOR mechanistic studies have been limited to Pt and Pt-Ru catalysts, and the so-called dual pathways proposed are summarized in Scheme 1, in which the CO pathway (or indirect pathway) is dominant on Pt in acidic solution while the non-CO pathway (or direct pathway) is minor.[10-17] Based on a density functional theory (DFT) study, the relative contribution for a specific pathway may heavily depend on whichever C-H or O-H bond cleavage initializes in the dehydrogenation of methanol,[18] that is, the initial cleavage occurring at the O-H bond favors the non-CO pathway while that at the C-H bond favors the CO pathway, as suggested for the MOR on Pt.

Scheme 1. Dual pathways proposed for MOR on Pt electrodes in acidic solutions.[11-14]

It is known that the oxidation of adsorbed CO proceeds via the Langmuir-Hinshelwood mechanism between CO_{ad} and OH_{ad} , the latter is formed from H_2O dissociation.[19, 20] Along this line, Pt-Ru alloys, being capable of facilitating dehydrogenation of methanol on Pt sites and dissociation of H_2O on more oxophilic Ru sites at lower potentials, i.e., by means of the so-called bifunctional mechanism, are very straightforward in promoting the CO pathway for MOR.[21-25] Although the weakened CO adsorption on Pt-Ru due to the electronic effect may additionally assist the MOR,[26-28] the bifunctional mechanism is widely regarded as the overwhelming one.[29, 30] The enhancement of MOR via the promoted CO pathway with Ru alloying was supported by in situ IR spectroscopy[31-34] and on-line differential electrochemical mass spectrometry (DEMS) measurement. [35, 36] Nevertheless, an interesting ATR-SEIRAS (surface enhanced IR absorption spectroscopy) investigation in conjunction with isotope labeling by Tong's group suggested a revised bifunctional mechanism for MOR at lower oxidation potentials that the non-CO pathway may otherwise be accounted for.[37]

To date, without prior relevant investigations, the classical bifunctional mechanism has been arbitrarily extended to explain the promoted MOR on Pt-metal oxide composites (MO_x), i.e., an alternative type of promising catalysts, assuming that the adsorbed CO on Pt sites can be readily scavenged by abundant hydroxyl species at the exposed Pt-metal oxide boundary,[38, 39] i.e.,

However, the simple extension of the mechanism to a different type of catalysts lacks direct molecular-level evidences. In other words, the validity of the bifunctional mechanism via promoting the dominant CO reaction pathway for MOR on Pt-MO_x should be clarified through qualitative and at least semi-quantitative analysis of the intermediates and products. It is noted that the ATR-SEIRAS is sensitive for detecting surface species but not so for the dissolvable ones, while the latter may be otherwise conveniently detected by on-line DEMS.

In this work, Pt-decorated SnO₂ nanoflakes supported on reduced graphene oxide (Pt-SnO₂/rGO) were designed to represent a typical Pt-MO_x composite catalyst with its structural and electronic features carefully characterized. This catalyst design takes the advantages of relative higher conductivity of nanostructured metal oxide, richer Pt-SnO₂ boundaries and higher Pt utilization. In situ ATR-SEIRAS together with on-line DEMS were applied to probe the MOR on Pt-SnO₂/rGO and Pt/C catalysts, with a focus on probing potential-dependent intermediates and products. In addition, DFT calculations are carried out to provide the energy diagrams for consecutive steps of methanol adsorption and oxidation reaction on the two model catalytic surfaces. Based on the comparative and comprehensive studies, a revised mechanism for the enhanced MOR on Pt-MO_x catalysts is proposed.

2. Experimental sections

2.1 Synthesis of Pt-SnO₂/rGO

SnO₂ nanoslices were prepared by a solvothermal method.[40, 41] Typically, 230 mg SnCl₂·2H₂O was firstly dissolved in 6 mL of absolute ethanol, followed by adding 80 mL of ethylenediamine and stirring for 20 min at 1000 rpm. The mixture was then transferred into 150 mL Teflon-lined autoclave and heated at 180 °C for 48 h. The white SnO₂ precipitate was collected by centrifuging, washed with absolute ethanol, and dried in vacuum at 65 °C for 10 h.

CO reduction method was used to prepare the Pt-SnO₂ nanoflakes.[42, 43] Briefly, 9 mg of SnO₂ was homogeneously dispersed in 200 mL of ultrapure water by ultrasonication, and stirred at 1000 rpm in oil bath at 60 °C for 3 h with CO bubbling. Then 10 mL of 5 mM K₂PtCl₄ was added dropwisely into the CO-saturated mixture by using a peristaltic pump at 500 μL min⁻¹. The mixture was kept under stirring and CO bubbling for another 2 h. At last, rGO aqueous slurry was added to the above Pt-SnO₂ colloid solution and kept stirring for 12 h. The Pt-SnO₂/rGO was collected by filtering, and washed with DI water and dried in vacuum at 65 °C for 10 h. The control reference of Pt/rGO sample was prepared in the same manner just at the absence of SnO₂ nanoslices.

2.2 Material Characterization

The morphology and microstructure of prepared materials were characterized by transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin microscope) equipped with an energy-dispersive spectrometer (EDS). X-ray diffraction (XRD) patterns were recorded on Bruker D8 Advance using Cu K α radiation from 10° to 90°. The electron binding energy and valence state of elements were investigated by PHI5000 ESCA X-ray photoelectron spectroscopy (XPS) system using Mg K α radiation (1253.6 eV). The composition of catalyst was analyzed by ICP-AES (Thermo Fisher iCAP 7400). Atomic force microscopy (AFM) measurements were carried on Bruker Dimension Icon.

The X-ray adsorption fine structure (XAFS) spectra at Pt L₃ edge (E_0 : 11564.0 eV) were recorded at room temperature at beam line BL14W1 of Shanghai Synchrotron Radiation Facility (SSRF), China. The BL14W1 was operated at the energy of 3.5 GeV with a constant current of 260 mA. The pure Pt foil was measured in transmission mode using ion chambers for energy calibration, while the other samples were conducted in the fluorescent mode with Lytle ion chamber detector. The IFEFFIT software (Athena and Artemis) was employed to analyze the obtained XAFS spectra.[44, 45] The EXAFS spectra were based upon k^3 -weight Fourier transforms. The fitting parameters for extended X-ray absorption fine structure (EXAFS) spectra included: coordination number (CN), interatomic distance (R), Debye Waller factor (σ^2), and correction-of-edge energy (ΔE_0).

2.3 Electrochemical measurements

All the electrochemical measurements were conducted using electrochemical workstation (Model 605B, CH Instruments, Inc.). A saturated calomel electrode (SCE) and a platinum mesh were used as the reference electrode and counter electrode, respectively. The working electrode was prepared by dropping 10 μ L of homogeneous catalysts ink (2 mg catalyst dispersed in 1 mL water/isopropanol solution (at a mass ratio of 1:4) with 20 μ L of 0.5 wt % Nafion) on a glass carbon rotating disk electrode (RDE) with the diameter of 5.0 mm.

The working electrode was activated in 1 M HClO₄ solution by cyclic voltammetry (CV) scans from 0.05 V to 1.25 V at a scan rate of 50 mV/s until a stable voltammogram was obtained. The MOR measurements were carried out in 1 M HClO₄ + 1 M CH₃OH solution by CV scans from 0.05 V to 1.25 V at a sweep rate of 50 mV/s with a rotation rate of 1600 rpm. The MOR stability test was performed in 1 M HClO₄ + 1 M CH₃OH solution by chronoamperometry at 0.70 V. The electrochemical surface area of catalyst was measured in 1 M HClO₄ solution by CO-stripping experiments within the potential window of 0.05 V to 1.25 V, at sweep rate of 10 mV/s. All the experiments were operated at room temperature, all the electrolytes were deoxygenated by N₂ bubbling and all potentials were measured against SCE and converted to against RHE except special instruction in this study.

2.4 In situ ATR-IR measurements

The in-situ ATR-IR measurements were conducted using a Nicolet iS50 FT-IR spectrometer equipped with a MCT detector cooled by liquid nitrogen, at a spectral resolution of 4 cm^{-1} and with p-polarized IR radiation. The working electrode was prepared by casting 200 μL of catalyst ink (see electrochemical measurements above) onto a Au-coated Si prism and then assembled in a spectroelectrochemical cell with a carbon rod as counter electrode and a SCE as reference electrode. ICP-AES results suggest the Pt mass loading to be 11.23% for Pt-SnO₂/rGO and 20% for JM Pt/C, therefore, the actual Pt mass loading on the working electrode was 0.055 mg/cm^2 for Pt-SnO₂/rGO and 0.10 mg/cm^2 for JM Pt/C, respectively. All spectra were converted into absorbance defined as $-\log(I/I_0)$, in which I and I_0 represent sample spectra and reference spectrum respectively. Dynamic potential scan was controlled by electrochemical workstation (Model 440C, CH Instruments, Inc.) at a sweep rate of 10 mV/s. The Au film on Si prism was prepared by a chemical deposition method as detailed in our previous works.[46-48]

2.5 On line DEMS measurements

The DEMS measurements were carried out using a home designed ‘probe-type’ quadrupole mass spectrometer (QMG220, Pfeiffer Vacuum, Inc.). The MS system and sleeving flow cell are illustrated in Figure S1. The internal capillary, made of 1.6-mm PTFE tubing and covered by a PTFE membrane (20 nm pore diameter, 50 μm thickness, and 50% porosity, Gore-Tex), was placed at 10 μm away from the surface of working electrode. The distance between the probe and the electrode was finely tuned by a micrometer screw gauge and directly viewed by a digital microscope with an objective at 10- μm resolution. The 8-mm branched external glass tube was connected to a peristaltic pump with a electrolyte flow rate of 1.25 mL min^{-1} during the measurement. The working electrode was prepared by dropping 10 μL of catalysts onto 3-mm glassy carbon electrode, a high-purity carbon rod and a SCE were used as counter electrode and reference electrode, respectively.

During DEMS measurements, CV scans were conducted at sweep rate of 5 mV/s and the ionic currents were recorded by the mass spectrometer. The calibration constant K^* is defined as $K^* = n Q_{\text{MS}} / Q_{\text{F}}$ or $K^* = n I_{\text{MS}} / I_{\text{F}}$, where n represents the number of electrons transferred in the redox reaction; Q_{MS} (I_{MS}) means mass spectrometric charge (current); and Q_{F} (I_{F}) is faradaic charge (current). The calibration constant K_{44}^* of both catalysts were derived from monolayer CO_{ads} stripping tests in 1 M HClO₄ solution, and their CVs and MSCVs were shown in Figure S2, respectively. After the monolayer CO_{ad} stripping test in 0.1 M HClO₄, a calculated volume of pure methanol was added into the HClO₄ solution to have the methanol concentration at 1 M for methanol electro-oxidation reaction experiments without any change in DEMS setup.

The faradaic charge Q_F , and the certain ion charge Q_{MS} , were obtained by integrating the CV of MOR and the corresponding MSCV in the cycle of potential sweep between 0.60 V and 1.25 V. Then the charge of the formation of CO_2 during MOR was calculated as $Q_F^*(44) = 6 Q_{MS}(44) / K^*(44)$, where the $Q_F^*(44)$ is the faradaic charge of CO_2 formed in the potential sweep cycle during MOR, $Q_{MS}(44)$ is the integrated ion charge for CO_2 during the potential sweep, 6 is the number of electrons for each methanol molecule oxidized to CO_2 , $K^*(44)$ is the calibration constant which was determined from CO_{ads} stripping before the MOR measurement on the same DEMS setup.

The average current efficiency of CO_2 in the cycle of potential sweep was determined as $A_q = Q_F^*(44) / Q_F$, where A_q is the average current efficiency of CO_2 , $Q_F^*(44)$ is the calculated faradaic charge of CO_2 product, Q_F is the overall faradaic charge from the whole cycle of potential sweep.

2.6 Computational Methods

All the DFT calculations were carried out by using the Vienna Ab-initio Simulation Package (VASP) along with the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA).[49-55] The project-augmented wave (PAW) pseudopotentials were utilized to represent the core-valence electron interaction.[56] The cut-off energy was set to be 450 eV and a $3 \times 3 \times 1$ Monkhorst-Pack k-point sampling was used for Brillouin zone. The close packed Pt-SnO₂ surface was modeled by $p(3 \times 2)$ unit cell with two layers. The two layers were relaxed during all optimization processes. The vacuum region layers were $\sim 18 \text{ \AA}$ to ensure the slab interaction was eliminated. A constrained optimization technique was employed to locate the transition states where the force converge criteria were limited to less than 0.05 eV/ $\text{\AA}$. [57-59] The adsorption energy was defined as: $E_{ad} = E(ad/surface) - E(ad) - E(surface)$, where $E(ad/surface)$, $E(ad)$, and $E(surface)$ are the total energies of the optimized adsorbates/surface system, gas molecules and the clean surface, respectively.

3. Results and Discussion

SnO₂ nanoflakes were employed as the substrate for growing Pt overlayers from a Pt(II) precursor solution, with CO gas serving as the complexing, reducing and terminating agent.[42, 43] Then the obtained Pt-SnO₂ composites were dispersed on reduced graphene oxide (rGO), with their TEM images shown in Figure 1A and Figure S3. Additional TEM, AFM and BET surface area characterizations of pristine SnO₂ could be found in Figures S4 to S8. Figure 1B shows the histogram of projected sizes of Pt-SnO₂ nanoflakes, presenting a mean value of ca. 2.5 nm. The EDS mapping and line scan profile as shown in Figures 1C-1E confirm that the Pt layer was coated on the ultrathin SnO₂. The AFM image of the Pt-SnO₂ nanoflakes dispersed on a mica sheet shown in Figure 1G reveals that majority of the Pt-SnO₂ nanoflakes exhibited the height from 1.35 to 1.65 nm. It is noted that due to the convolution of the

cantilever tip and a nanoscale sample, the measured height is relatively accurate while the lateral distance may be artificially enlarged without a clear-cut edge, as well as partial agglomeration of Pt-SnO₂ nanoflakes on atomic-smooth surface of mica sheet.

Figure 1. (A) TEM image and (B) size distribution of Pt-SnO₂/rGO, (C) EDS mapping and (D-E) EDS line-scan profiles of Pt-SnO₂, (F) AFM image of Pt-SnO₂ (the inserted numbers with the unit nm represent the heights along with the white lines) and (G) representative height profiles on the marked nanoflakes in (F).

Figures 2A and 2B show the XPS patterns for Pt 4f and Sn 3d regions of a commercial (Johnson Matthey) Pt/C, Pt/rGO, Pt-SnO₂/rGO and SnO₂/rGO, using the C 1s binding energy at 284.6 eV as the reference. Compared to the counterparts for Pt/C and Pt/rGO, both the Pt 4f_{5/2} and Pt 4f_{7/2} XPS peaks

for Pt-SnO₂/rGO shifted to lower values. In contrast, the Sn 3d_{3/2} and Sn 3d_{5/2} binding energies were positively shifted. Therefore, the negative shift of Pt 4f binding energies could be attributed to partial electron transfer from SnO₂ to Pt.

To further investigate the electronic structure and coordination environment of Pt atoms, the X-ray absorption spectra (XAS) at Pt L₃ edge were recorded. As shown in Figure 2C, the intensity of white line (WL) for Pt atoms shows in the order of Pt-SnO₂/rGO < Pt/C. The WL in L₃ edge reflects the degree of unoccupied d-symmetry orbitals (5d) above the Fermi level, relating to the oxidation state of Pt atoms.[60, 61] This relatively lower WL intensity for the Pt-SnO₂/rGO was consistent with the above XPS result of partial electron transfer from SnO₂ to Pt. The extended X-ray absorption fine structure (EXAFS) spectra with corresponding fitting results are shown in Figure 2D and Table S1. The lower coordination number of Pt-O for Pt-SnO₂/rGO also confirms a lower oxidation state of Pt with respect to that for Pt/C. As shown in Table S1, the similar Pt-Pt distance (2.71 Å) suggests a negligible difference in Pt lattice strain on both Pt-SnO₂/rGO and Pt/C. Hence, the major difference between the two catalysts is the significant electronic effect between Pt and SnO₂.

Figure 2. XPS for Pt 4f region (A) and Sn 3d region (B); Pt L₃ edge XANES spectra (C) and EXAFS spectra with fitting results (D) for commercial Pt/C and Pt-SnO₂/rGO

The cyclic voltammograms for Pt-SnO₂/rGO and Pt/C in 1 M HClO₄ and 1 M HClO₄ + 1 M CH₃OH are shown in Figure S9A and Figure 3A. Both the onset and peak potentials for MOR on Pt-SnO₂/rGO show a negative shift of ca. 50 mV as compared to the counterparts on Pt/C. In addition, the Pt-

SnO₂/rGO exhibited a much higher peak current density, that is 21.76 A m⁻² (or 1.31 A mg⁻¹_{Pt}), which is 3.62 (or 2.47) times of 6.01 A m⁻² (or 0.53 A mg⁻¹_{Pt}) obtained on Pt/C and 2.13 (or 1.98) times of 10.20 A m⁻² (or 0.66 A mg⁻¹_{Pt}) obtained on Pt/rGO as shown in Figure 3B and Figure S10A. Notably, similar electrocatalytic properties of Pt/rGO and Pt/C towards MOR were observed, validating the important role played by the electronic effect in Pt-SnO₂ as indicated by the above XPS and XAFS characterizations. In Figure 3C, the chronoamperometric curves recorded at 0.70 V (vs. RHE), show that the current density from Pt-SnO₂/rGO is 5.32 A m⁻², which is 4.70 times of that from Pt/C (1.13 A m⁻²). These results clearly demonstrate that Pt-SnO₂/rGO possesses a much higher poisoning-tolerance than Pt/C. In Figure S9B, virtually no significant electrochemical surface area (ECSA) change was observed after the chronoamperometric MOR test, suggesting a good structural stability of Pt-SnO₂/rGO. Figure 3D and Figure S10B shows the CO stripping voltammograms, in which the peak potential of CO_{ad} removal on Pt-SnO₂/rGO is significantly lower than that on Pt/C and Pt/rGO. The electrochemical surface areas (ECSA) of Pt-SnO₂/rGO and Pt/C were also evaluated from the CO stripping charge and found to be 60.19 m² g⁻¹ and 88.33 m² g⁻¹, respectively. Furthermore, Pt-SnO₂/rGO delivers a peak current density 2 times higher and a *j*_{3600s} 1.6 times higher than that on state-of-the-art PtRu/C catalyst with a similar oxidation onset potential (Figure S10C and S10D). A comprehensive summary and comparison of MOR performances on Pt-SnO₂/rGO, other Pt-MO_x and PtRu from this work and recent published data are listed in Table S2, it can be seen clearly that the promising electrocatalytic properties manifest that the as-synthesized Pt-SnO₂/rGO can be representative of high performance Pt-MO_x composite catalysts for the targeted study.

Figure 3. Electrocatalytic performance of the Pt-SnO₂/rGO and commercial Pt/C. (A) CVs in 1 M HClO₄ + 1 M CH₃OH at a scan rate of 50 mV/s; (B) Histograms of the peak current density data

normalized by either Pt mass loading or ECSA taken from Panel A; (C) Chronoamperometric curves recorded at 0.70 V (vs. RHE) in 1 M HClO₄ + 1 M CH₃OH; (D) CO monolayer stripping curves recorded in 1 M HClO₄ at a scan rate of 10 mV/s.

In-situ ATR-SEIRAS spectroscopy study was carried out to explore the evolution of interfacial species, at the molecular level, during MOR on these two catalysts. The acquired spectra are presented in Figure 4. The linearly adsorbed CO (CO_L) species on Pt/C were observed with the potential-dependent IR band at 2013 ~ 2055 cm⁻¹, together with the much weaker band at ~1790 cm⁻¹ arising from the small amount of bridge-bonded CO (CO_B). The IR band at ~1325 cm⁻¹ can be assigned to the symmetric OCO stretching mode of bridge-bonded formate (HCOO_B). Also noted is that the band around 1675 cm⁻¹ may be due to multi-bonded CO or interfacial hydronium, and the band at ~1610 cm⁻¹ due to the bending mode δ (HOH) of interfacial water. Detailed IR peak assignments are listed in Table S3. The IR band intensities of CO_L and HCOO_B on Pt/C and Pt-SnO₂/rGO as a function of potential are compared in Figures 4C and 4D, together with the measured cyclic voltammograms starting from 0.05 V. The formate and CO species are highly relevant to the two reaction pathways for MOR. In general, a much weaker (ca. 1/15th) CO band, and a relatively stronger (ca. 1.5 folds) HCOO_B band, were observed on Pt-SnO₂/rGO than on Pt/C, that is, the relative band intensity of HCOO_B to CO on Pt-SnO₂/rGO is > 20 times higher than that on Pt/C, and > 16 times higher than that on Pt/rGO (Figure S11). In the positively-going potential sweep, the CO_L band intensity decreased significantly at relatively lower potentials on Pt-SnO₂/rGO than on Pt/C, being largely consistent with different onset oxidation potentials. The much weaker CO band could be ascribed to the initially far less CO formation from methanol dissociation on Pt-SnO₂/rGO at 0.05 V before the start of potential cycling. On the other hand, it was reported that HCOO_B may be a reactive intermediate in favor of the further oxidation of HCOOH (an intermediate product of MOR in acidic solution).[11] Alternatively, HCOO_B could re-orient to monodentate formate to facilitate further C-H cleavage to produce CO₂, having a lower activation energy.[62, 63] With these understandings in mind, the relative stronger HCOO_B band does match with the higher MOR activity on Pt-SnO₂/rGO, as can be found in Figure 4. In other words, as compared to the MOR on Pt/C, the enhanced direct pathway via formate as reactive intermediate can be feasible on Pt-SnO₂/rGO.

Figure 4. In situ ATR-SEIRAS spectra for (A) commercial Pt/C and (B) Pt-SnO₂/rGO in 1 M HClO₄ + 1 M CH₃OH with a time resolution of 5 s, using a single-beam spectrum at open circuit potential in 1 M HClO₄ as the reference spectrum; the artefact band around 1235 cm⁻¹ is due to the Si-O stretching of SiO_x. Corresponding CVs of (C) Pt/C and (D) Pt-SnO₂/rGO at a scan rate of 10 mV/s with the integrated band intensities of CO_L and HCOO_B. Current densities were normalized by geometric electrode area of 0.785 cm², and a constant catalyst loading was used for ATR-SEIRAS measurements, leading to an actual Pt mass loading of 0.1 mg_{Pt}/cm² for Pt/C and 0.055 mg_{Pt}/cm² for Pt-SnO₂/rGO.

To investigate volatile intermediates and products distribution during MOR, an on-line DEMS system was designed (see Experimental section for details). Prior to MOR investigation, the DEMS measurement for anodic CO adlayer stripping was carried out as a calibration experiment for CO₂ detection, according to the procedures outlined by Baltruschat and Koper.[12, 35] Cyclic voltammograms (CVs) and mass cyclic voltammograms (MSCVs), as shown in Figure 5A, reveal that both catalysts yielded a similar response of ion currents to the faradaic currents. The ion currents (I_{MS}) of $m/z = 44$ and 60 correspond to CO₂ and methyl formate (HCOOCH₃), respectively; the latter being arisen from the reaction of the HCOOH intermediate with CH₃OH in the solution, which generally served as the indicator of the amount of HCOOH being generated. The average current efficiency of electro-oxidation of methanol to CO₂ was ca. 78.6% on Pt-SnO₂/rGO and 66.4% on Pt/C, as determined from three independent experiments; suggesting the composite catalyst promoted the total methanol

oxidation to CO_2 . Note that the absolute I_{MS} was affected by the collection efficiency of each measurement setup, therefore, we calculated the relative ratio of methyl formate to CO_2 ($I_{\text{MS},60}/I_{\text{MS},44}$) on the same catalyst of Pt/C versus that on Pt-SnO₂/rGO, and plotted them in Figure 5B to highlight the difference in the formate pathway. The $I_{\text{MS},60}/I_{\text{MS},44}$ ratio on Pt-SnO₂/rGO is about 4 times higher than that on Pt/C, and 2.60 times higher than that on Pt/rGO (Figure S12). Moreover, the $I_{\text{MS},60}$ on Pt-SnO₂/rGO increased significantly at a lower potential of 0.50 V, as compared to that on Pt/C. Taken together the higher overall CO_2 current efficiency on Pt-SnO₂ surface, it can be deduced that the formate pathway contributed mainly to this enhanced activity. This DEMS result is consistent with the above ATR-SEIRA data where a stronger HCOO_B band and a weaker CO_L band were observed throughout the potential window on Pt-SnO₂/rGO as compared to Pt/C.

Figure 5. Simultaneously recorded CVs and MSCVs for $m/z = 44$ and $m/z = 60$ on (A) commercial Pt/C and Pt-SnO₂/rGO in 1 M HClO_4 + 1 M CH_3OH at scan rate 5 mV/s. The corresponding potential-dependent plot of (B) the relative ratio of $I_{\text{MS},60}/I_{\text{MS},44}$ as measured from 0.60 V to 1.20 V. A constant catalyst loading was used for the DEMS measurement, leading to an actual Pt mass loading of 4.0 μg_{Pt} for Pt/C and 2.3 μg_{Pt} for Pt-SnO₂/rGO.

These rich and first hand *in-situ* IR and on-line DEMS data reveal clearly, at the molecular level, that the SnO₂ nanoflakes modified by Pt adlayer promotes methanol oxidation via a direct formate pathway, whilst inhibiting the methanol dissociation to CO_{ads}. In order to further explain the above observations, we performed first-principle simulations using DFT calculations, with the details of the modelled structures shown in Figure S13. For MOR on modelled Pt-SnO₂ surface, Pt adlayer was assumed to form a metal chain bridging at the coordinatively unsaturated Sn sites and oxygen at bridge sites, and SnO₂ sites were saturated by H₂O/OH.[64] The energy profiles for methanol dehydrogenation over Pt-SnO₂ are presented in Figure 6A. Table S4 summarises the activation barriers and reaction energies for each process over Pt-modified SnO₂. From these data, it is found that the direct pathway via formate as reactive intermediate appears to be plausible, as shown by a low energy barrier of 0.39 eV for the last elemental reaction to form formic acid and a much higher barrier of 0.62 eV for the CO* formation. Therefore, the preferred reaction pathways on Pt-SnO₂ can be described as:

CH₃OH* → CH₃O* → CH₂O* → CHO* → HCOOH*. This result is well correlated with the increase in the HCOO_B band intensity in the *in-situ* ATR-SEIRAS study and the higher $I_{MS,60}/I_{MS,44}$ ratio in the online DEMS measurement. Thus both the experimental data and the DFT calculations provide supportive evidences that MOR over Pt-SnO₂ prefers the direct formate pathway. Moreover, further decomposition of adsorbed HCOOH followed Langmuir-Hinshelwood surface reaction mechanism. HCOOH_{ads} firstly dissociated to form H* and bidentate HCOO_B* with a facile barrier of 0.44 eV, followed by the HCOO_B* transforming to monodentate HCOO_M* by overcoming 0.38 eV barrier, the latter decomposed into CO₂ and H* with a feasible barrier of 0.47 eV. In fact, the proposed HCOOH* decomposition agrees with the studies of formic acid oxidation reaction over Pd and Pt[62, 65, 66] where the catalytic decomposition of formic acid could be rather viable over Pt-SnO₂.

For comparison, the energy profiles for methanol dehydrogenation on Pt(111) are presented in Figure 6B, while the details of activation barriers and reaction energies are listed in Table S5. Over Pt(111), the reaction pathways are different from the ones over Pt-SnO₂, which can be described as:

CH₃OH* → CH₂OH* → CHOH* → CHO* → CO*. In addition, it is seen that the activation energy of each step of methanol oxidation over Pt-SnO₂ is more facile than the corresponding one over Pt(111), indicating that the methanol dehydrogenation over Pt-SnO₂ is more favored, both kinetically and thermodynamically. The decrease in the activation barrier is consistent with the experimentally observed enhancements in both the specific activities and the average current efficiency of CO₂ formation from the MOR over Pt-SnO₂ /rGO.

Figure 6. Potential energy profiles of methanol adsorption and oxidation reaction over (A) Pt-SnO₂ and (B) Pt(111) surfaces. The red lines highlight the preferred formate reaction pathway on Pt-SnO₂ and the preferred CO pathway on Pt (111), respectively.

4. Conclusion

In summary, we have prepared interface-rich Pt-SnO₂ nanoflakes (ca. 2.5 nm) supported on reduced graphene oxide as an efficient type of Pt-metal oxide hybrid catalyst for electrocatalytic methanol oxidation reaction (MOR). Significant electronic structure modification on Pt in contact with SnO₂, concomitant with enhanced MOR, has been revealed by ex-situ XPS and XAFS data. Combined studies of in-situ ATR-SEIRAS and on-line DEMS provide clear evidences, at molecular level, that the non-CO pathway involving formic acid-formate intermediates is selectively enhanced on Pt-SnO₂ compared to the CO pathway which prevails on Pt. DFT calculations further reinforce that this electronic structure manipulation contributes mainly to the reaction route tuning towards an enhanced MOR via the non-CO pathway. This comprehensive study of MOR on a model catalyst of Pt-metal oxide nanocomposites, with new insights into relevant reaction mechanism, will pave the way for more efficient MOR catalyst design, and in turn promotes future advancement of direct methanol fuel cells.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, including material characterizations, electrochemical measurement data, IR peak assignments and calculated reaction barriers.

Declarations of interest: none.

Credit Author Statement

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Acknowledgements

This work was supported by the NSFC (Grant No. 21733004) of MOST, the International Cooperation Program of STCSM (Grant No. 17520711200), the National Basic Research Program of China (973 Program, 2015CB932303), the EPSRC (EP/I013229/1), the Royal Society and the Newton Fund (NAF\R1\191294). K.J. acknowledges the support from Shanghai Sailing Program (Grant No. 20YF1420500). We thank Drs. Linlin Wei and Xin Wang from Bruker Corporation for the atomic force microscope (AFM) tests. We would like to acknowledge the beamline BL14W1 (Shanghai Synchrotron Radiation Facility) for providing the beam time.

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