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โครงการ การเพิ่มขนาดปรากฏการณ์เนมคา (NEMCA) ในเครื่องปฏิกรณ์แบบแพคเบดสำหรับการออกซิไดซ์โพรเพน

โดย พลัง บำรุงสกุลสวัสดิ์

30 มิถุนายน 2560

สัญญาเลขที่ TRG5880223

รายงานวิจัยฉบับสมบูรณ์

โครงการ การเพิ่มขนาดปรากฏการณ์เนมคา (NEMCA) ในเครื่องปฏิกรณ์แบบแพคเบดสำหรับการออกซิไดซ์โพรเพน

ผู้วิจัย พลัง บำรุงสกุลสวัสดิ์
สังกัด ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัยและต้นสังกัด

Abstract

Project code: TRG5880223

Project title: Scale-up of NEMCA effect in packed-bed reactors for propane oxidation

Investigator: Palang Bumroongsakulsawat, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University

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Project period: two years

Non-faradaic Electrochemical Modification of Catalytic Activity (NEMCA) of propane oxidation at Pt dispersed on yttria-stabilized zirconia (YSZ) discs by strong electrostatic adsorption (SEA) and wet impregnation (WI) in wireless configuration was studied and compared. With a stoichiometric gas mixture of propane and oxygen diluted in helium, an exceptionally large faradaic yield of 5.2×10^4 was achieved from a cell prepared by SEA at a reaction temperature of 200 °C and a cell voltage of 6 V, compared to a smaller value of 1.0×10^4 obtained from a cell prepared by WI. A conceptual mechanism explaining the dependence of the faradaic yields and the rate enhancement ratios on Pt particle sizes is proposed.

งานวิจัยนี้ศึกษาปรากฏการณ์เนมคา (Non-faradaic Electrochemical Modification of Catalytic Activity, NEMCA) ของปฏิกิริยาการออกซิไดซ์โพรเพนที่พลาตินัมที่กระจายบนวายเอสเซด (yttria-stabilised zirconia, YSZ) ด้วยวิธีการดูดซับด้วยไฟฟ้าสถิตย์อย่างแรง (strong electrostatic adsorption, SEA) และการเคลือบฝังแบบเปียก (wet impregnation, WI) ในรูปแบบไร้สาย ด้วยแก๊สผสมโพรเพนและออกซิเจนที่อัตราส่วนตามสัมประสิทธิ์ปฏิกิริยาและเจือด้วยฮีเลียม เซลล์ที่เตรียมด้วยการดูดซับด้วยไฟฟ้าสถิตย์อย่างแรงให้ค่าผลได้ฟาราเดอิก (faradaic yield) 5.2×10^4 ที่ 200 องศาเซลเซียส และความต่างศักย์ 6 โวลต์ ในขณะที่เซลล์ที่เตรียมด้วยการเคลือบฝังแบบเปียกให้ค่าเป็น 1.0×10^4 คณะวิจัยได้เสนอกลไกที่ทำให้ค่าผลได้ฟาราเดอิกขึ้นอยู่กับขนาดอนุภาคพลาตินัมด้วย

Keywords: NEMCA; EPOC; propane; electrochemical promotion

1 Objectives

Pt is an active metal for numerous reactions including the oxidation of hydrocarbons and is thus incorporated in catalytic converters to facilitate the oxidation of residual light hydrocarbons as a means of pollution control. However, the rising price of the precious metal calls for more efficient use of the catalyst. Increasing the catalytic activity of Pt through NEMCA is one of a few available solutions and could reduce Pt loadings in catalytic converters.

NEMCA is a process by which, when electric potential differences are imposed on two or more catalyst electrodes separated by an electrolyte, the catalytic rate of the formation of a product at one or more electrodes is enhanced above that which could possibly be attained were the system to behave entirely faradaically. Briefly, the imposed potential differences induce the migration of ions from the electrolyte to the catalyst electrode or vice versa, causing changes in the work function of the catalyst, altering the adsorption characteristics of reactants, thereby modifying the reaction rates.

Two parameters are used to quantify NEMCA: faradaic yield and rate enhancement ratio. The former can be calculated by the following equation:

$$\Lambda = \frac{r - r_0}{I / nF} \qquad \text{E1}$$

where Λ is the faradaic yield;

r is the observed reaction rate;

r_0 is the observed reaction rate at open-circuit;

n is the charge of the conducting ion;

F is the faraday constant,

and the latter by the following expression:

$$\rho = \frac{r}{r_0} \qquad \text{E2}$$

where ρ is the rate enhancement ratio.

$|\Lambda| > 1$ confirms the presence of NEMCA, while the rate enhancement ratio indicates the extent of rate modification. The values of faradaic yields depend on several factors including but not limited to catalyst, electrolyte, reaction, and temperature and can be as large as 10^5, but are generally in the orders of 10^2-10^3.

One of the difficulties in the implementation of NEMCA arises from the wiring in NEMCA systems, of which a conventional configuration in Figure 1a requires the direct contact between the catalyst electrode and the wire. This conventional configuration is preferred in kinetic studies mainly due to the unidirectional changes in the work function of the catalyst during polarization. The catalyst electrode needs to form a continuous phase of electronic conductivity in order to achieve uniformly distributed electric potential. Therefore, conventional studies of this phenomenon are conducted with a relatively thick layer of sintered Pt paste on a YSZ disc, which is wasteful and therefore impractical for commercial implementation.

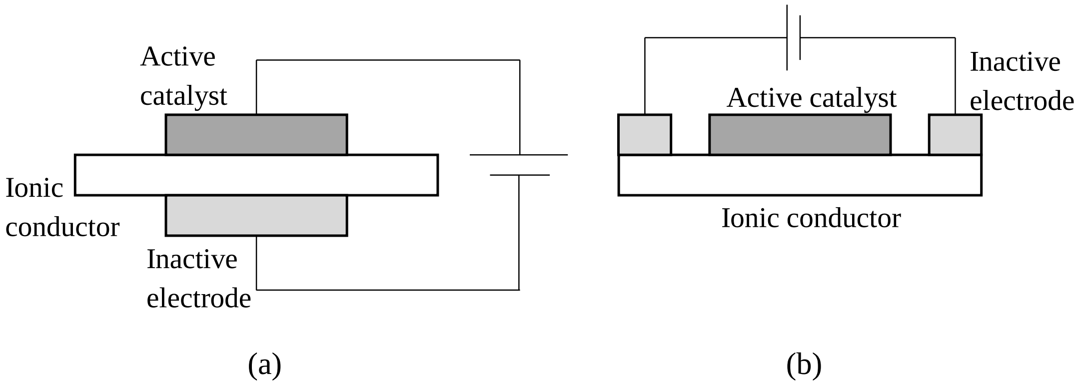

Figure 1 Schematic diagram of two wiring configurations in NEMCA studies: conventional (a) and wireless (b).

On the other hand, electric potential differences can also be imposed on the catalyst remotely through distant electrodes shown in Figure 1b. This configuration is termed 'wireless' due to the absence of the direct contact between the catalyst and the wire. The exact mechanism of how NEMCA occurs in this configuration is still unclear but a limited number of NEMCA studies conducted in wireless configuration suggest that the catalyst clusters deposited on the electrolyte function as bipolar electrodes. As wireless configurations do not require the catalyst layer to be in a single continuous phase of high electrical conductivity, a catalyst can be dispersed as fine particles on an ionic conductor for more effective use of precious metals.

This paper presents the NEMCA of propane oxidation, which is employed to model the oxidation of light hydrocarbons in exhaust gas, with exceptionally high faradaic yields at Pt-impregnated YSZ in wireless configuration.

2 Methodology

2.1 Cell preparation

Au was sputtered on two equal opposite segments on the same side of a YSZ disc of 20-mm diameter and 1.2-mm thickness to form two inert electrodes. A 10-mm-wide stripe of bare YSZ was left in the middle for Pt deposition by SEA or WI to achieve the same Pt loading of 1.2 µmol m^{-2}.

2.2 Pt deposition by SEA

Strong electrostatic adsorption (SEA) is a technique for catalyst deposition developed by Regalbuto's team, who showed that the technique offered superior metal dispersion. Briefly, the pH of a solution containing a catalyst precursor is adjusted with respect to the point of zero charge (PZC) of a substrate so that the charge on the surface of the substrate in contact with the precursor solution is opposite of the charge of the metal precursor ions in order to achieve maximum attraction between the two. The technique was employed to achieve finely dispersed Pt on YSZ in this work.

2.2.1 Determination of suitable conditions for Pt deposition on YSZ powder by SEA

2.2.1.1 pH-shift experiments

The point of zero charge (PZC) of the substrate must be determined to narrow down suitable pH through a series of pH-shift experiments. 850 mg of YSZ powder (Inframat Advanced Materials), of which the measured BET surface area was 58.6 m2 g^{-1}, was added to 50 ml DI water of different pH pre-adjusted with dilute HNO_3 or NaOH solutions to form suspensions with surface loadings of 10^3 m^2 L^{-1}. The suspensions were shaken for 1 h, after which equilibrium adsorption was assumed. The final pH was measured and plotted against the initial pH to show the plateau indicating the PZC of YSZ, which was found to be 5. Therefore, the surface of YSZ was positively charged and negatively charged in aqueous solutions of pH below 5 and above 5, respectively. As chloroplatinate was chosen as the Pt precursor in this work, the optimum pH of the precursor solution for the deposition should lie below 5.

2.2.1.2 Adsorption experiments

Two series of adsorption experiments were carried out at a constant Pt precursor concentration and a constant pH to find the optimum equilibrium pH and the optimum Pt precursor concentration, respectively, for the deposition. In either cases, 850 mg YSZ powder was added to 50 ml aqueous solutions containing Pt from $H_2PtCl_6{\cdot}6H_2O$ (Aldrich). The experiments in the former series were conducted at a constant Pt atoms concentration of 200 ppm but different initial solution pH below 5, while those in the latter were at the optimum pH determined previously but different Pt atom concentrations. The suspensions were shaken for 1 h, after which the concentrations of Pt atoms in the aqueous solutions were analysed by ICP-AES to calculate the amounts adsorbed on the YSZ powder. The optimum equilibrium pH and the optimum equilibrium Pt atom concentration were found to be 3 and 64 ppm, respectively. The maximum adsorption of Pt on YSZ at these conditions was 1.2 μmol m^{-2}.

2.2.2 Pt deposition on YSZ discs by SEA

Because the specific surface area of a YSZ disc is extremely smaller than that of YSZ powder, the changes in the concentration of the Pt precursor and the pH are not expected to be detectable after the equilibrium adsorption is reached with a YSZ disc. Therefore, the composition of a solution for the deposition of Pt on a YSZ disc was that at the final state of the optimum equilibrium adsorption determined previously with YSZ powder (pH 3 and atomic Pt concentration of 64 ppm). A YSZ disc with the irrelevant areas masked was submerged in 50 ml of this solution for 1 h, and then dried overnight in flowing air. The masks were removed and the cell was reduced at 250 °C with H_2 for 2 h. The surface Pt concentration on the YSZ disc, i.e. moles of Pt per active area of the disc, was assumed to be identical to that obtained with YSZ powder at 1.2 μmol m^{-2}.

2.3 Pt deposition on YSZ discs by WI

An aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ was prepared so that 100 μL of this solution contains the entire amount of Pt required on a YSZ disc to achieve the same surface metal concentration as that of the cell prepared by SEA. 100 μL of this solution was poured on the unmasked area between the two Au electrodes on a YSZ disc and left to dry overnight in flowing air. After the masks were removed, the cell was reduced at 250 °C with H_2 for 2 h.

2.4 Reactor configuration

A prepared cell was connected to a power supply with two Au wires at the two sputtered Au electrodes. The cell was then placed in a quartz vessel inside a furnace and positioned directly next to the exit of the gas inlet. A gas mixture consisting of 0.27 kPa C_3H_8 + 1.35 kPa O_2 (stoichiometric ratio for complete combustion) in He was fed to the quartz vessel by setting appropriate flow rates of 3% C_3H_8 in He, 10% O_2 in He, and 99.999% He (Linde). The product stream from the quartz vessel was analysed by an online IR spectrometer for CO_2 concentrations, which could be converted to rates of CO_2 formation.

3 Results and discussion

Figure 2 presents the faradaic yields and the rate enhancement ratios from cells prepared by both SEA and WI at cell voltages up to 30 V at 200 °C. The highest faradaic yield of 5.2×10^4 was achieved in this work at a cell voltage of 6 V from the cell prepared by SEA. The value then gradually decreased to 1.4×10^4 as the cell voltage was increased to 30 V. The rate enhancement ratio of this cell correspondingly rose from 1.0 and levelled off at 3.7 as the cell voltage was increased. The largest faradaic yield in this work is one of the highest values from propane oxidation at Pt-YSZ. Systems with wireless configurations rarely achieve faradaic yields beyond 10^3.

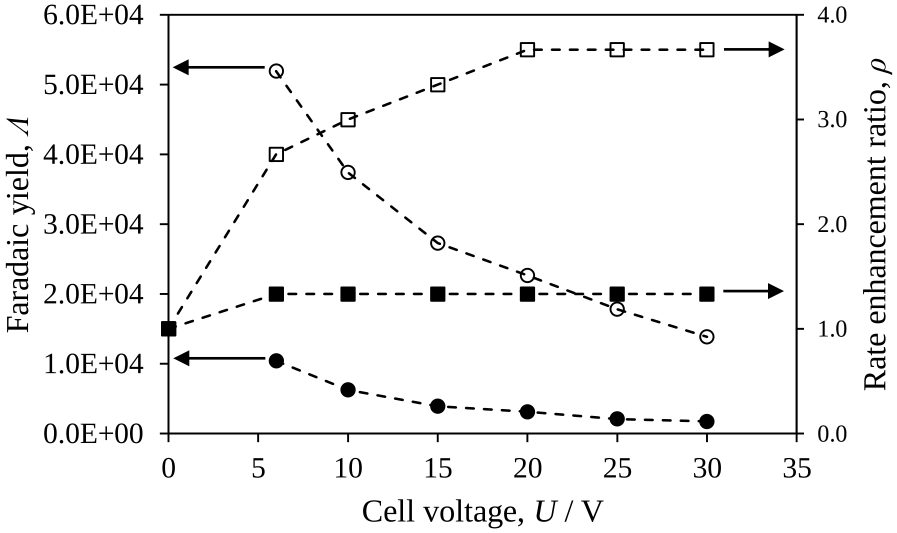

Figure 2 Dependence of faradaic yields (circles) and rate enhancement ratios (squares) on applied cell voltages from cells prepared by SEA (hollow marks) and WI (filled marks) at 200 °C

On the other hand, the cell prepared by WI exhibited poorer performance. Its highest faradaic yield was obtained at 6V and smaller than its counterpart by a factor of 5. Nevertheless, this value was still astonishingly high. The value then decreased and presumably approached zero as the cell voltage was increased to 30 V. The rate enhancement ratios of this cell increased only slightly to 1.3.

The results (Figure 2) suggest that the reaction rates from the cell prepared by SEA were more sensitive to cell voltages than those from the cell prepared byWI. As the procedures for the deposition of Pt on YSZ discs by both SEA and WI were designed to achieve the same surface concentration, another characteristic might be the cause of the differences in the results. YSZ powder with Pt deposited by SEA and WI with the same surface concentration of 1.2 μmol m^{-2} were prepared for CO chemisorption to find the dispersion of Pt, which were determined to be 81% and 44%, respectively. The values indicated that the SEA technique truly offers smaller Pt particle sizes than the conventional WI technique. Pt particle sizes seem to influence faradaic yields and rate enhancement ratios through a novel mechanism, which is developed and hypothesised here.

The Pt particles on a NEMCA cell in wireless configuration are thought to function as bipolar electrodes. Therefore, the work function should be increased in one region and decreased in the other of each Pt particle. As propane oxidation under similar conditions exhibits the electrophobic behaviour, the reaction rates should be enhanced and suppressed, respectively, in those regions.

Figure 3 depicts Pt particles of two sizes on YSZ functioning as bipolar electrodes. The cell is polarised cathodically on the left and anodically on the right. O_2 in the gas mixture is reduced at the Au electrode on the left (i). The product O^{2-} migrates to the right against the electric field in the YSZ (ii) and is oxidized to O^2 at the Au electrode on the right (iii). Although the highly conductive Pt particles have no electric field inside, i.e. having uniformly distributed electric potential inside, they are in contact with YSZ with a potential gradient. Hence, Pt particles act as bipolar electrodes, oxidizing some O^{2-} in the YSZ on their left (iv). The oxidized species, $O^{\delta-}$, is strongly adsorbed on the Pt particles and diffuses on the Pt surfaces toward the right (v), forming strong effective electrical double-layer around the left regions of the Pt particles and enhancing rates of electrophobic reactions. Some of this species may be desorbed as O_2 along the path (vi), but the remaining $O^{\delta-}$ arriving at the right of the Pt particles as well as O_2 in the gas mixture are reduced by the electrons that the Pt particles gain from the oxidation to O^{2-} (vii), which is then transferred to the YSZ. This process depletes the strongly adsorbed $O^{\delta-}$ on the right regions of the Pt particles, suppressing rates of electrophobic reactions. As a result, polarization creates on each Pt particle two adjacent regions of rate enhancement and rate suppression for electrophobic reactions.

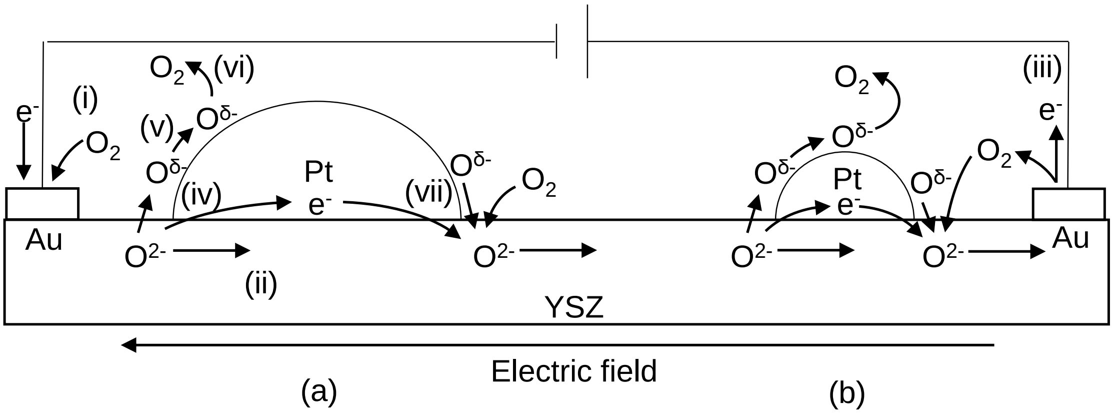

Figure 3 Pathways of oxygenic species in a polarised cell in wireless configuration (not to scale): large catalyst particle (a) and small catalyst particle (b)

As adsorbed $O^{\delta-}$ can travel on the surface of Pt particles only for some distance before it is desorbed as O_2, a smaller Pt particle has a larger fraction of the surface densely covered by $O^{\delta-}$ for rate enhancement than a larger Pt particle. Thus, the cell with smaller Pt particles fabricated with SEA showed larger faradaic yields and rate enhancement ratios.

4 Conclusion

Working wireless NEMCA cells have been fabricated and a large faradaic yield of 5.2×10^4 was achieved from the cell fabricated with SEA at 200 °C and a cell voltage of 6 V. A mechanism for the dependence of the faradaic yields and the rate enhancement ratios on Pt particle sizes is proposed.

5 Recommendation

The new insight about the dependence of the faradaic yields on catalyst particle sizes should be incorporated in new designs of NEMCA reactors.

Appendix

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High Faradaic Yields of Non-Faradaic Electrochemical Modification of Catalytic Activity of Propane Oxidation at Pt-YSZ

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Non-faradaic Electrochemical Modification of Catalytic Activity (NEMCA) of propane oxidation at Pt dispersed on yttria-stabilized zirconia (YSZ) discs by strong electrostatic adsorption (SEA) and wet impregnation (WI) in wireless configuration was studied and compared. With a stoichiometric gas mixture of propane and oxygen diluted in helium, an exceptionally large faradaic yield of 5.2×10^4 was achieved from a cell prepared by SEA at a reaction temperature of 200°C and a cell voltage of 6 V, compared to a smaller value of 1.0×10^4 obtained from a cell prepared by WI. A conceptual mechanism explaining the dependence of the faradaic yields and the rate enhancement ratios on Pt particle sizes is proposed.

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Pt is an active metal for numerous reactions including the oxidation of hydrocarbons and is thus incorporated in catalytic converters to facilitate the oxidation of residual light hydrocarbons as a means of pollution control. However, the rising price of the precious metal calls for more efficient use of the catalyst. Increasing the catalytic activity of Pt through NEMCA is one of a few available solutions and could reduce Pt loadings in catalytic converters.

NEMCA is a process by which, when electric potential differences are imposed on two or more catalyst electrodes separated by an electrolyte, the catalytic rate of the formation of a product at one or more electrodes is enhanced above that which could possibly be attained were the system to behave entirely faradaically. This phenomenon was discovered unexpectedly by Vayenas and his then student, Stoukides.[1,2] The most plausible mechanism of the process is published elsewhere.[3,4] Briefly, the imposed potential differences induce the migration of ions from the electrolyte to the catalyst electrode or vice versa, causing changes in the work function of the catalyst, altering the adsorption characteristics of reactants, thereby modifying the reaction rates.

Two parameters are used to quantify NEMCA: faradaic yield and rate enhancement ratio.[3,4] The former can be calculated by the following equation:

$$\Lambda = \frac{r - r_0}{I/nF} \qquad [1]$$

where Λ is the faradaic yield

r is the observed reaction rate
r_0 is the observed reaction rate at open-circuit
n is the charge of the conducting ion
I is the measured electric current
F is the faraday constant

and the latter by the following expression:

$$\rho = r/r_0 \qquad [2]$$

where ρ is the rate enhancement ratio.

$|\Lambda| > 1$ confirms the presence of NEMCA, while the rate enhancement ratio indicates the extent of rate modification. The values of faradaic yields depend on several factors including but not limited to catalyst, electrolyte, reaction, and temperature and can be as large as 10^5, but are generally in the orders of 10^2–10^3.[3]

One of the difficulties in the implementation of NEMCA arises from the wiring in NEMCA systems, of which a conventional configuration in Figure 1a requires the direct contact between the catalyst electrode and the wire. This conventional configuration is preferred in kinetic studies mainly due to the unidirectional changes in the work function of the catalyst during polarization. The catalyst electrode needs to form a continuous phase of electronic conductivity in order to achieve uniformly distributed electric potential. Therefore, conventional studies of this phenomenon are conducted with a relatively thick layer of sintered Pt paste on a YSZ disc, which is wasteful and therefore impractical for commercial implementation.

On the other hand, electric potential differences can also be imposed on the catalyst remotely through distant electrodes shown in Figure 1b. This configuration is termed ‘wireless’ due to the absence of the direct contact between the catalyst and the wire.[5,6] The exact mechanism of how NEMCA occurs in this configuration is still unclear but a limited number of NEMCA studies conducted in wireless configuration suggest that the catalyst clusters deposited on the electrolyte function as bipolar electrodes.[5–12] As wireless configurations do not require the catalyst layer to be in a single continuous phase of high electrical conductivity, a catalyst can be dispersed as fine particles on an ionic conductor for more effective use of precious metals.

Strong electrostatic adsorption (SEA) is a technique for catalyst deposition developed by Regalbuto et al.,[13,14] who showed that the technique offered superior metal dispersion. Briefly, the pH of a solution containing a catalyst precursor is adjusted with respect to the point of zero charge (PZC) of a substrate so that the charge on the surface of the substrate in contact with the precursor solution is opposite of the charge of the metal precursor ions in order to achieve maximum attraction between the two. The technique was employed to achieve finely dispersed Pt on YSZ in this work.

Propane oxidation is employed in this paper as a model reaction of the oxidation of light hydrocarbons in catalytic converters. NEMCA of this reaction has been studied at sintered metal paste on YSZ,[15–19] sputtered metals on YSZ,[20–23] sintered Pt paste on β''-Al_2O_3,[24,25] and LSM-YSZ.[26] All of these experiments were conducted in the conventional configuration (Figure 1a). Most of the reported faradaic yields were in the orders of 1–10^3 except that from Billard and Vernoux,[20] which reached an astonishing value of 1.2×10^6. The reported rate enhancement ratios of this reaction rarely exceeded 4, but the values reported by some groups were in the order of 10^2 and beyond 10^3 in some conditions.[16–18]

This paper presents unexpectedly and unusually high faradaic efficiencies of NEMCA of propane oxidation at Pt-impregnated YSZ in wireless configuration.

Experimental

Au was sputtered on two equal opposite segments on the same side of a YSZ disc of 20-mm diameter and 1.2-mm thickness to form two inert electrodes. A 10-mm-wide stripe of bare YSZ was left in the middle for Pt deposition by SEA or WI to achieve the same Pt

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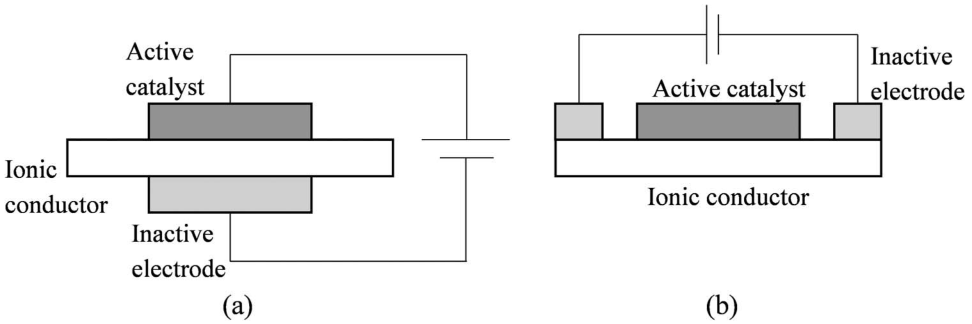

Figure 1. Schematic diagram of two wiring configurations in NEMCA studies: conventional (a) and wireless (b).

loading of 1.2 μmol m^{-2}. The procedures for the deposition of Pt by both methods are described in the supplementary material.

A prepared cell was connected to a power supply with two Au wires at the two sputtered Au electrodes. The cell was then placed in a quartz vessel inside a furnace and positioned directly next to the exit of the gas inlet. 0.27 kPa C_3H_8 + 1.35 kPa O_2 (stoichiometric ratio for complete combustion) in He was fed to the quartz vessel by setting appropriate flow rates of 3% C_3H_8 in He, 10% O_2 in He, and 99.999% He (Linde). The product stream from the quartz vessel was analyzed by an online IR spectrometer for CO_2 concentrations, which could be converted to rates of CO_2 formation.

Results and Discussion

Figure 2 presents the faradaic yields and the rate enhancement ratios from cells prepared by both SEA and WI at cell voltages up to 30 V at 200°C. The highest faradaic yield of 5.2×10^4 was achieved in this work at a cell voltage of 6 V from the cell prepared by SEA. The value then gradually decreased to 1.4×10^4 as the cell voltage was increased to 30 V. The rate enhancement ratio of this cell correspondingly rose from 1.0 and levelled off at 3.7 as the cell voltage was increased. The largest faradaic yield in this work is one of the highest values from propane oxidation at Pt-YSZ and probably second only to the work of Billard and Vernoux in which a value of 1.2×10^6 was reported,[20] while common values are generally in the orders of 10^2–10^3.[16–19,21] Systems with wireless configurations rarely achieve faradaic yields beyond 10^3.[5–7]

On the other hand, the cell prepared by WI exhibited poorer performance. Its highest faradaic yield was obtained at 6 V and smaller than its counterpart by a factor of 5. Nevertheless, this value was still astonishingly high. The value then decreased and presumably approached zero as the cell voltage was increased to 30 V. The rate enhancement ratios of this cell increased only slightly to 1.3.

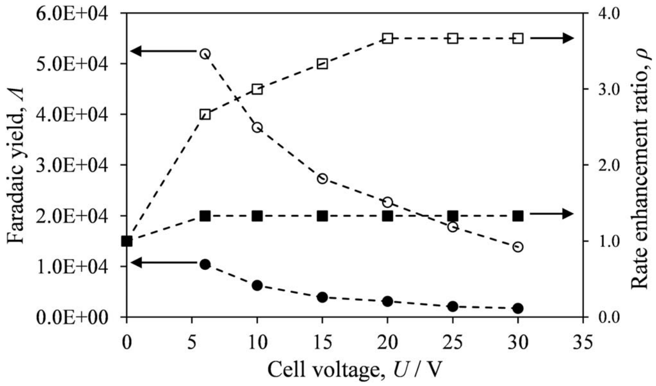

Figure 2. Dependence of faradaic yields (circles) and rate enhancement ratios (squares) on applied cell voltages from cells prepared by SEA (hollow marks) and WI (filled marks) at 200°C.

The large cell voltages up to 30 V employed in this work is, if not never, rarely used anywhere else. In wireless configuration, the current flows from one terminal to the opposite on the same side of a disc. Distribution of current densities is expected within the YSZ disc and probably depends on the geometry of the whole cell including the arrangement of the functioning parts on the disc. As the catalyst deposited on a YSZ disc can only sense the current density directly beneath itself, NEMCA performance depends on cell geometry and arrangement. Unfortunately, this information is rarely clearly defined in papers describing NEMCA experiments, especially in wireless configuration. Thus, the cell voltages required to induce NEMCA effects could vary significantly from one experimental set-up to another and should not be directly compared.

The results (Figure 2) suggest that the reaction rates from the cell prepared by SEA were more sensitive to cell voltages than those from the cell prepared by WI. As the procedures for the deposition of Pt on YSZ discs by both SEA and WI were designed to achieve the same surface concentration, another characteristic might be the cause of the differences in the results. YSZ powder with Pt deposited by SEA and WI with the same surface concentration of 1.2 μmol m^{-2} were prepared for CO chemisorption to find the dispersion of Pt, which were determined to be 81% and 44%, respectively. The values indicated that the SEA technique truly offers smaller Pt particle sizes than the conventional WI technique. Pt particle sizes seem to influence faradaic yields and rate enhancement ratios through a novel mechanism, which is developed and hypothesized here.

According to the bipolar electrode concept proposed by Marwood et al.,[5–12] the work function should be increased in one region and decreased in the other of each Pt particle on YSZ. As propane oxidation under similar conditions exhibits the electrophobic behavior,[15,19–23] the reaction rates should be enhanced and suppressed, respectively, in those regions.

Figure 3 depicts Pt particles of two sizes on YSZ functioning as bipolar electrodes. The cell is polarized cathodically on the left and anodically on the right. O_2 in the gas mixture is reduced at the Au electrode on the left (i). The product O^{2-} migrates to the right against the electric field in the YSZ (ii) and is oxidized to O_2 at the Au electrode on the right (iii). Although the highly conductive Pt particles have no electric field inside, i.e. having uniformly distributed electric potential inside, they are in contact with YSZ with a potential gradient. Hence, Pt particles act as bipolar electrodes, oxidizing some O^{2-} in the YSZ on their left (iv). The oxidized species, $O^{\delta-}$, is strongly adsorbed on the Pt particles and diffuses on the Pt surfaces toward the right (v), forming strong effective electrical double-layer around the left regions of the Pt particles and enhancing rates of electrophobic reactions. Some of this species may be desorbed as O_2 along the path (vi), but the remaining $O^{\delta-}$ arriving at the right of the Pt particles as well as O_2 in the gas mixture are reduced by the electrons that the Pt particles gain from the oxidation to O^{2-} (vii), which is then transferred to the YSZ. This process depletes the strongly adsorbed $O^{\delta-}$ on the right regions of the Pt particles, suppressing rates of electrophobic reactions. As a result, polarization creates on each Pt particle two adjacent regions of rate enhancement and rate suppression for electrophobic reactions.

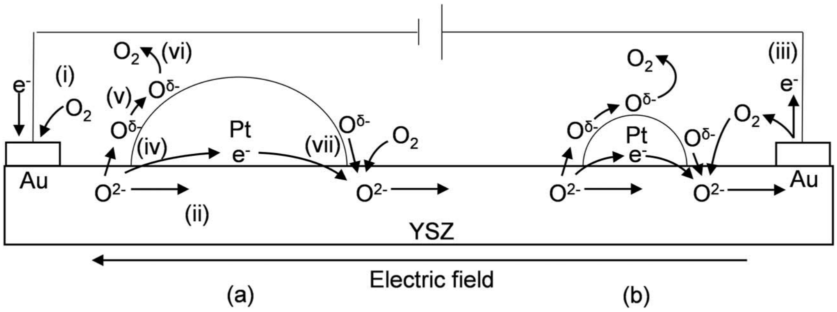

Figure 3. Pathways of oxygenic species in a polarized cell in wireless configuration (not to scale): large catalyst particle (a) and small catalyst particle (b).

As adsorbed $O^{\delta-}$ can travel on the surface of Pt particles only for some distance before it is desorbed as O_2, a smaller Pt particle has a larger fraction of the surface densely covered by $O^{\delta-}$ for rate enhancement than a larger Pt particle. Thus, the cell with smaller Pt particles fabricated with SEA showed larger faradaic yields and rate enhancement ratios.

Summary

A large faradaic yield of 5.2×10^4 was achieved from the cell fabricated with SEA at 200°C and a cell voltage of 6 V. A mechanism for the dependence of the faradaic yields and the rate enhancement ratios on Pt particle sizes is proposed.

Acknowledgments

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