Vol. 50 Commemorative Highlight Review

Inorganic Nanocatalysts for Hydrogenation Reactions Contributable to a Sustainable Material Supply

Miho Yamauchi1,2
1International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
2Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan
E-mail: yamauchi@i2cner.kyushu-u.ac.jp

Miho Yamauchi received her Ph. D under the guidance of Professor Ryuichi Ikeda from University of Tsukuba in 2001 and started research works as a technical staff there. She moved to Kyushu University as an assistant professor in 2003 and to Catalysis Research Center, Hokkaido University as an associate professor in 2008. In 2012, she joined International Institute for Carbon-Neutral Energy Research, Kyushu University as a PI and became a professor in 2017. Her research interests involve hydrogen related properties of metal and alloy nanoparticles, selective catalysis on the structure controlled oxide catalysts and electrocatalysis for sustainable material production.

Abstract

Hydrogenation reactions using non-fossil-based hydrogen sources upgrade ubiquitous molecules to useful chemicals with low environmental load and can be promoted on nanoscale inorganic catalysts (nanocatalysts). This review discusses determining factors that enhance the catalytic activity and selectivity of thermal and electrochemical hydrogenation reactions using nanocatalysts, of which the reactivity is dependent on their electronic states, atomic arrangements and surface structures.

Keywords: Hydrogenation | Nanoalloy | Titanium dioxide

Introduction

Hydrogenation reactions that convert ubiquitous chemicals such as N₂ and CO₂ to useful feedstocks directly or indirectly using renewable energy and non-fossil resources will compose essential industrial processes to achieve sustainable material supplies under the control of lower CO₂ emissions. Such hydrogenation reactions are classified into three types; thermal hydrogenation reactions (THR), photochemical hydrogenation reactions (PHR) and electrochemical hydrogenation reactions (EHR). Figure 1 represents the equilibrium potentials of the hydrogenation reactions to produce NH₃ from N₂, ethylene and ethanol from CO₂, glycolic acid from oxalic acid, lactic acid from pyruvic acid and alanine from pyruvic acid oxime; these potentials are calculated using thermodynamic quantities. Although these six hydrogenation reactions are thermodynamically favorable compared to H₂ production from water, we sometimes need to apply a considerable large amount of thermal or electrical energy to initiate these reactions; thus, catalysts designed to reduce the energy input are highly desired. PHRs used in by “artificial photosynthesis” are inseparable from water splitting and great achievements have been made in this area. Such

![Figure 1](image-url)
achievements have been reviewed by various authors and are beyond the scope of this paper. This review focuses on one THR and two EHRs: the THR of ammonia synthesis and EHRs of CO₂ and carboxylic acid (or carbonyl), which will play significant roles in the realization of a hydrogen-based society, carbon recycling and carbon-neutral energy circulation, respectively. Nanoscale inorganic catalysts (nanocatalysts) composed of metals or oxides are widely used in various catalytic reactions due to their large reactive surface area, favorable durability and high designability. Herein, this review determines the electronic states and elemental arrangements of nanocatalysts that enhance the catalytic performance of THRs and EHRs by referring to recent reports.

Metal nanoparticles (NPs) that interact strongly with the supporting materials show excellent catalytic performances distinguishable from those in bulk metals, as Haruta reported CO oxidation on Au NPs supported on TiO₂.² Highly active NP catalysts have a Fermi level located in proximity to the frontier orbitals of reactant molecules; this phenomenon has been elucidated by intensive theoretical research.³ Alloying is a simple but effective technique for modifying the reactivity of NPs through electronic (ligand) and geometric (ensemble) effects.⁴ The energy band of nanoscale alloys (nanoalloys, NAs) tends to become narrower⁵ and the center of gravity of the d-band, i.e., “d-band center”,⁶ shifts to a higher energy⁷ due to limitation of the domain size for homogeneous metal, resulting in a larger density of states compared to those of simple metal NPs having a similar particle size and enhancement in catalytic activity.⁴ The most extreme example is single-atom alloys.⁸ The structures of NAs are classified into three types, solid-solution (random, Figure 1c), ordered (intermetallics, Figure 1d)⁹ and phase separated types (Figure 1e). Ordered NAs exhibit a distinctive band structure (Figure 1d), which is different from those of pure metal NPs (Figures 1b and 1e), whereas solid-solution NAs (Figure 1c) have a textureless band structure that reflects the averaged occupancies of the component atoms.¹⁰ The band structures of phase-separated NAs reflect those of the component metals (Figure 1e). Catalytic reactions are basically local events between reactant molecules and a few atoms on the surface, and these elemental arrangements can influence the catalytic performance.

Metal oxide semiconductors, which are characterized by specific band gap energies, play a critical role in photocatalytic reactions. Recently, oxide catalysts have been applied as electrocatalysts due to their high durability and activity under harsh conditions, such as highly acidic or alkaline conditions.¹¹,¹² In general, oxide nanocatalysts show relatively high overpotentials for electrochemical H₂ evolution compared to those on metals, which is a great advantage in EHRs for the production of chemicals other than H₂. Alloying modifies the electronic states of the oxides (Figures 1g and 1h) and can be a controlling factor for EHRs. This review introduces recently developed functions of metal and oxide nanocatalysts to provide clues for the further creation of efficient catalysts.

Ammonia Synthesis Catalysts (NH₃ THRs) Created from New Concepts

Ammonia synthesis (AS) via the Haber-Bosch (H-B) process is the most economically feasible process as long as one can use high temperature (400–600 °C), high pressure (20–40 MPa) and H₂, which are generated via the reforming of cheap natural gas.¹³ Recently, ammonia synthesized using H₂ produced from natural gas in combination with enhanced oil recovery-based carbon capture and storage, called “blue” ammonia, has drawn great attention as a carbon-neutral hydrogen carrier. However, ammonia produced from non-fossil chemicals and renewable energies, i.e., “green” ammonia, should be used to achieve substantial carbon-neutral hydrogen supplies in the future. However, if green hydrogen, such as electrolytic hydrogen, is used, the H-B process loses its economic merits at present. This is because extra energy is consumed to attain high temperature and high pressure. Therefore, the development of novel AS catalysts that work under milder conditions with sufficient durability is a critical challenge.

**Hydride Catalysts.** In the H-B process, Fe-based catalysts supported on Al₂O₃ (H-B catalysts) have been applied and can work for 30 years without maintenance. The outstanding usability of the H-B catalyst has minimized the need for the development of new AS catalysts. Recently, Kitano discovered considerably high AS activities on Ru-loaded hydride catalysts in which the hydride support suppresses hydrogen poisoning on the metal surface.¹⁴ This finding has reinvestigated the development of AS catalysts, by enhancing support functions such as electron donation,¹⁵ hydrogen spillover,¹⁶ and hydrogen storage.¹⁷ Intensive studies extend the utilization of various kinds of hydride supports, such as LiH¹⁷ and TH₂.¹⁸

**Oxide-supported Catalysts Exhibiting Strong Metal Support Interactions (SMSIs).** Aika discovered Ru based AS catalysts¹⁹ and found that the application of promoters drastically enhances the AS activities of Ru catalysts.²⁰ He further pointed out the importance of the interaction between the support and metal catalysts for AS, i.e., strong metal support interaction (SMSI).²¹,²² Recently, Nagaoka prepared highly active Ru based AS catalysts supported on La₂₋₅Ce₀.₅O₃.₇₅ by applying high temperatures, which enhanced the reduction of Ce⁴⁺ ions in the support and electron transfer from the support to Ru catalysts. Furthermore, the highest AS performance has been achieved using nonprecious Co catalyst via encapsulation by BaO supported on MgO, a which is activated at a high temperature.²³

**Atominically Mixed Nanoalloy Catalysts.** Alloying is the simplest but still a useful methodology to improve catalytic performance. In AS systems, NA catalysts have not been fully examined. Efficient catalysts exhibit a balanced adsorption/desorption behavior among reactants, intermediates and products, which is well known as the Sabatier principle. Studies based on density functional theory (DFT) propose the concept of describing the catalytic performance based on the scaling relation.²⁴ The difference in product selectivity likely comes from the difference in binding energies (Ēₘ) of the intermediate species.³ Ru and Fe are known to bind with N weakly and strongly, respectively. In terms of the scaling relationship,²⁵ the Ėₘ of the central element of an intermediate species on the catalyst scales the activation energy. Thus, RuFe NAs are expected to show moderate interactions with N and afford a feasible catalyst surface for AS reactions. Although well-mixed solid solution RuFe NAs are not easily prepared because of the large difference in reduction potentials between Ru and Fe, the simultaneous precipitation on the support enables atomic level mixing of Ru and Fe (Figure 2a),²⁶,²⁷ which maximizes the
interaction between constituent elements. RuFe NAs supported on MgO (RuFe/MgO), for which the amount of metal loading was 1.5 wt.%, apparently exhibited higher activity at temperatures above 500 °C than Ru catalysts supported on MgO (Ru/MgO with a loading amount of 2 wt.%), as shown in Figure 2b. Interestingly, the reaction orders both for N₂ and H₂ on RuFe/MgO were positive (Figure 2d), whereas that for H₂ on Ru/MgO was negative (Figure 2c). DFT studies indicated that the d-band center for RuFe NAs is located between those for Ru and Fe (Figures 2e–2g), which leads to appropriate adsorption states of reactant molecules for AS reactions. Furthermore, the threefold degenerate t₂g states are more responsive than the 2-fold degenerate e₃g states for the narrower d-band near the d-band center on the RuFe NAs. This appropriately tuned d-band of the alloy catalyst makes it highly active for NH₃ production. The metal d-band structure significantly changes upon H adsorption due to the interaction with the H s orbital; this indicates the strength of the H–catalyst interaction. Upon the interaction with H, the density of states for the lowest part of the d-band reaches a maximum on the Ru catalyst and is reduced on the RuFe NAs; the change in the band structure accounts for the negative reaction order of Ru/MgO and higher hydrogen poisoning tolerance of RuFe/MgO. Although electronic states cannot perfectly predict reactivities on the real catalyst surface, knowledge of the contributions from electronic states helps to optimize the catalyst functions.

**Electrochemical Hydrogenation Reaction of CO₂ (CO₂ EHR) to Produce Green Carbon Feedstocks**

Catalyst development for CO₂ EHRs has been underway for over 30 years. Hori is one of the pioneers for the development of catalysts for CO₂ EHRs and clarified that the product selectivity in EHRs largely depends on the constituent metal element. Simple metal catalysts are classified into 4 types; these include catalysts with selectivity for the production of formic acid, H₂, CO, HCOO⁻, and often involves Cu (Figure 3).²⁹,³⁰ Cu shows exceptional abilities for CO₂ EHRs, because it produces various chemicals, including hydrocarbons and alcohols, and therefore suffers from lower product selectivity. Cu-based CO₂ EHR catalysts with both high activity and high selectivity do not currently exist.

**Mechanistic Understanding for CO₂ EHRs.** DFT-based studies have succeeded in organizing the activity descriptors for CO₂ EHRs.²⁴ The CO₂ EHR for CH₄ production proceeds via the transfer of eight proto–electron pairs and results in seven adsorbed intermediates. The limiting potentials (ULs), at which each elementary step of a reaction becomes downhill in free energy, can be described as a function of the chemical potentials of the species bound to the catalyst surface, and the ULs for all elemental steps are scalable using one of the calculated Eₐ values, e.g., ULs are described as a function of Eₐ for adsorbed CO (Eₐ[CO]), as shown in Figure 4. Reactions proceed at potentials more negative than the equilibrium potential. Figure 4 clearly suggests that the overpotential for CH₄ production, which is the extra potential required over the equilibrium potential for the reaction, is ascribed to the COH* or CHO* formation.

**High Selectivity in the CO₂ EHRs on Atom-arrangement-controlled Nanoalloys (NAs).** Eₐ values for a reactant molecule are strongly influenced via the interaction with a few surface atoms; therefore, elemental arrangement can be an influential factor in a catalytic reaction. Pd shows a strong interaction with hydrogen,⁶ and alloying Pd within the Cu surface may change the product selectivity in CO₂ EHRs. Three
types of CuPd nanoalloy (NA) catalysts with different mixing patterns were prepared; these mixing patterns include disordered (or solid-solution), ordered (intermetallics) and phase-separated NAs. CuPd NAs with a B2-type ordered structure, which is the most stable under ambient conditions, were prepared by exposing disordered NAs to a H₂ atmosphere. Figure 5 shows the Faradaic efficiency (FE) of CuPd NAs, which is a percentage of electrons used for the generation of the product to the consumed electrons in the process and is correlated to the product selectivity. On the ordered B2 CuPd NAs, CO was the main product, whereas C2 chemicals such as ethylene and ethanol were preferentially produced on the phase-separated NAs. The disordered CuPd NAs showed an average product distribution between those on B2 and phase-separated NAs. It was proposed that the adsorbed CO on a Cu atom tends to form the CHO intermediate with the oxygen atom that is partially adsorbed on the Pd atom, which stabilizes the adsorption of the CHO intermediate. As the concentration of Cu changes from CuPd₁, CuPd to Cu₃Pd in increasing order while maintaining a disordered structure, the FE of the C₂ products increase. Thus, the neighboring Cu atoms on the phase-separated NAs may allow for adjacent adsorbed CO, which is dimerized easily to the CO₂ intermediate for the production of C₂ chemicals. These results imply that well-defined arrangements of active sites are required for high product selectivity on nanocatalysts.

Figure 4. Limiting potentials (U₁) for elementary proton-transfer steps in CO₂ EHRs. Each line is the calculated potential at which the indicated elementary reaction step is neutral with respect to free energy, as a function of the electrocatalysts’ carbon affinity, E₀[CO]. The equilibrium potential for the CH₄ formation (+0.17 V vs. RHE) is indicated by the broken line. Competitive pathways are indicated as lines of the same color, and the more favorable and less favorable routes are shown as solid and dotted lines, respectively. The binding energy where CO adsorbed on the surface is in equilibrium with 1% CO gas is shown as a vertical dotted line. The pen circles correspond to the surface that has an experimental current density in the hydrogen evolution reaction. The theoretical overpotential is given by the distance between the equilibrium line and the most-negative U₁ line (highlighted in gray). Reprinted with permission from ref 24. Copyright (2012) American Chemical Society.

Figure 5. Faradaic efficiency of CO₂ EHRs on CuPd NAs. Reprinted with permission from ref 32. Copyright (2017) American Chemical Society.

EHRs of Organic Acids on TiO₂-based Oxide Nanocatalysts for Carbon-neutral Fuel Recycling and Production of Value-added Chemicals

CO₂ EHRs have attracted much attention in terms of carbon recycling, although CO₂ capture and separation remains challenging. In nature, plants accumulate atmospheric CO₂ highly efficiently; hence, biderivable materials such as organic acids are also regarded as a low-carbon chemical resource. The efficient THRs of polar organic functionalities bearing fewer electrophilic carbonyl groups, such as carboxylic acids and their derivatives, are targets for synthetic organic chemistry due to their tremendous potential. TiO₂ is a widely used catalyst material due to its high activity and adequate stability. Interestingly, anatase TiO₂ was found to exhibit high activity for EHRs of oxalic acid (divalent carboxylic acid, HOOC-COOH, OX) to glycolic acid (monovalent alcohol, HOOC-CH₂OH, GC) in the following reaction scheme, which is described in the first report of the electrochemical reduction of carboxylic acids to produce an alcoholic compound. Cathode: HOOC-COOH + 4H⁺ + 4e⁻ → HOOC-CH₂OH + H₂O +0.13 V vs RHE.

Anode: 2H₂O → 4H⁺ + 4e⁻ + O₂ +1.23 V vs RHE.

Overall: HOOC-COOH + H₂O → HOOC-CH₂OH + O₂ 1.1 V

In this EHR system, GC is produced via 4-electron reduction of OX, which affords efficient electronic power storage into GC with a high volumetric energy density, 8,600 MJ m⁻³, cf., 13 MJ m⁻³ for H₂ gas.


Controlling the structures of TiO₂ is critical for EHRs of organic acids. Detailed analysis of the surface structure of active and inactive TiO₂ catalysts was conducted by scanning transmission electron microscopy (STEM) measurement com-
Figure 6. EELS maps of anatase and rutile phases on catalysts and energy diagrams of anatase- and rutile-type TiO$_2$. (a) and (c) STEM images of active and inactive catalysts for EHRs of oxalic acid. (b) and (d) EELS maps of active and inactive catalysts composed of Ti L3-edge signals in the area marked by squares in (a) and (c). The EELS signal intensities from the anatase and rutile phases are recognized by green and red colors, respectively. The dark area in an inactive catalyst shown in (d) indicates the weakened intensity of the beam caused by transmission through the thick center of catalyst. Illustrations for distributions of anatase and rutile phases in (e) active and (f) inactive catalyst. (g) Energy diagrams of conduction and valence bands for anatase- and rutile-type TiO$_2$ conduction and valence bands and redox potentials for the production of H$_2$ and GC. The grey and black squares represent conduction and valence bands, respectively, assuming that the flat-band potential is equal to the conduction-band edge potential. Reproduced from ref 37 with permission from The Royal Society of Chemistry.

EHRs on TiO$_2$ for the formation of nonaromatic organic acids such as saturated fatty acids, $\alpha$-keto acids and unsaturated fatty acids were examined using DFT calculations. Interestingly, in these groups, OX, $\alpha$-keto acids and fumaric acid were electrochemically reduced on the TiO$_2$ electrode. To understand this tendency, the HOMO and LUMO levels of the organic acid molecules were calculated. As shown in Figures 7a and 7b, $\alpha$-keto acids exhibit a hybridized LUMO orbital extended over the whole molecule, whereas the hybridization is limited only to the carboxylic group in saturated fatty acids. The well-extended hybridization not only lowers the LUMO level of $\alpha$-keto acids and OX (Figure 7c) but also affords multi-electron reduction by the electron transfer from an electrode to acids because of their sufficient capacities for electrons.

The interaction between the TiO$_2$ surface and an acid such as acetic acid (saturated acid), OX and glyoxylic acid (GO, $\alpha$-keto acid) was also investigated (Figure 7d). The orbital mixing between the LUMO of the acid and the conduction band of TiO$_2$ is strikingly different among the three acids. The orbital of the nonreactive acetic acid is localized only on the anchoring carboxylic group, whereas the empty conduction-band orbitals of TiO$_2$ extend to the LUMOs of the OX and GO molecules, which contain the oxo-groups. Furthermore, the amplitude of the acetic acid orbital is small, whereas those on OX and GO are considerably large, showing a strong orbital interaction in the latter cases. These results support that electrons from the electrode can smoothly transfer to the empty orbitals on the $\alpha$-carbon, i.e., highly developed hybridization between the orbitals of a catalyst surface and the LUMO of the substrate molecule enhances the electroreduction.

**Complex Oxide Electrodes for Efficient EHR of Organic Acids.** To optimize the energy state of TiO$_2$, alloying of anatase TiO$_2$ with Zr ions was examined. A Zr ion has a valence state similar to that of a Ti ion but has a larger ionic radius than that of a Ti ion, i.e., the ionic radii of Zr$^{4+}$ and Ti$^{4+}$ ions are 0.720 and 0.605 Å, respectively. Thus, the Zr ion appears to be feasible as a dopant to modify the electronic and structures of TiO$_2$. Ti-ZrO$_2$ complex oxide particles prepared via a solvothermal method showed an anatase structure up to $x = 0.15$ but became amorphous from $x = 0.2$ to 0.8. Both the conversion of OX and the FE for the production of GC were found to depend on the x values, as shown in Figure 8a. The FE
for the GC production was rapidly increased at $x = 0.1$ and decreased at $x = 0.15$, which implies that the crystal structure is deeply related to the OX activity. To clarify the reason for the composition dependence, the electronic states were examined as shown in Figure 8b. It is notable that CBB is rapidly increased at $x = 0.05$ and became constant above the Zr content. The higher CBB level seems to be advantageous for the reduction of substrates, which is one of the requisites for higher activity in the OX EHR. However, the rapid decrease at approximately $x = 0.15$ cannot be explained because amorphous Ti$_{1-x}$Zr$_x$O$_2$ particles possess higher CBB levels. The local structures were investigated by the atomic pair distribution function (PDF) analysis of synchrotron X-ray total scattering.\(^{35}\) Figure 8c presents the Zr content dependence of the distribution of the distance between metal and O ions (M-O distance) and FE for GC production. Surprisingly, the activities are well correlated with the M-O distribution. Thus, crystallinity of the oxide was found to significantly modify the EHR activities.

**Oxygen Evolution Reaction (OER) Enhanced on Amorphous IrO$_2$ Applied on TiO$_2$ for Efficient EHR.** In EHRs, protons and electrons are provided via water oxidation at an anode, i.e., the oxygen evolution reaction (OER), and therefore, the OER is indispensable for EHRs. Thus, a OER catalyst is introduced, although the OER is not a hydrogenation reaction. IrO$_2$ NPs are well known to show the high OER activity with considerable durability even in highly acidic media. TiO$_2$, which acts as a cathode for EHRs, is found to be stable as a support for IrO$_2$, enhancing its activity. IrO$_2$ NPs with $x < 2$ applied to a TiO$_2$ electrode (IrO$_2$/TiO$_2$) were prepared by chemical reduction using ethylene glycol in the presence of a TiO$_2$ electrode, where IrO$_2$ was not pure IrO$_2$ but instead contained metallic Ir (Figure 9a). The prepared electrode was found to show high OER activity with a considerably small overpotential, e.g., 1.43 V vs. RHE at 10 mA cm$^{-2}$.\(^{31}\) In contrast, IrO$_2$/TiO$_2$ calcined at 350 °C did not show good activity. Why did such enhancement occur on the pristine IrO$_2$/TiO$_2$? This question was answered through in-situ X-ray absorption spectroscopy (XAS), which was measured under applied potential. In the Ir LIII-edge X-ray absorption near-edge structure for active IrO$_2$/TiO$_2$, an absorption peak shifted to higher energy levels with applied potentials (Figure 9b). In contrast, no such potential dependence for the calcined inactive catalyst was observed (Figure 9c). Furthermore, IrO$_2$ NPs on the active (pristine) catalyst were found to exhibit low crystallinity, i.e., they are amorphous, and were surrounded by a considerable amount of -OH groups formed on the TiO$_2$ surface. These results imply that Ir ions in the IrO$_2$ NPs located on TiO$_2$ exhibit flexibly variable valency states, which contributed to the remarkably high OER activity because active Ir species with high valency (Ir$^{5+}$) are easily formed on amorphous IrO$_2$ NPs supported on TiO$_2$. The TiO$_2$ provides -OH species to compensate for the extra charges generated on the IrO$_2$ NPs when the potential is applied.

**Advanced Uses of EHRs of Organic Acids.** The high overpotentials generated in OERs are immensely problematic for EHRs. If light energy is introduced for the OER, the total applied potential for the EHRs can be reduced. In this regard, oxide photocatalysts were applied to the OER at the anode in an OX EHR.\(^{40}\) Notably, UV-visible light irradiation to a WO$_3$ photocathode enables the OX EHR to produce GC above 0.5 V, which is lower (by 0.6 V) than the theoretical bias, i.e., 1.1 V (Figure 10). GC electrolysers with an 80% high FE was achieved when a bias of 1.5 V was applied under UV-visible irradiation ($\lambda > 300$ nm). This is the first example of direct photoenergy storage into an alcoholic compound via the EHR of an organic acid.

Various $\alpha$-keto acids are electrochemically reducible to the corresponding hydroxides on a TiO$_2$ catalyst. One example is electrochemical lactic acid formation from pyruvic acid.\(^{38}\) Both lactic and pyruvic acids work in a glycolysis system in living organisms and can be used as biocompatible redox couples for thermo-electrochemical conversion (TEC). A TEC system employing a mixed solution of lactic acid and pyruvic acid and a Ti mesh electrode on which TiO$_2$ was grown (TiO$_2$/Ti mesh) exhibited TEC conversion with a positive Seebeck coefficient.

---

**Figure 8.** Faradaic efficiency (FE) of the productions of GC and glyoxylic acid (GO) and conversion of OX in electrochemical reduction of OX on Ti$_{1-x}$Zr$_x$O$_2$ particles at $-0.7$ V vs. RHE at 50 °C for 2 h. (b) Energy levels of the valence band top (VBT) and conduction band bottom (CBB) of the Ti$_{1-x}$Zr$_x$O$_2$ particles. (c) The distribution of Ti(Zr)-O distances and the FE for GC production as a function of Zr content, $x$. The dotted lines indicate a boundary between the anatase and amorphous phases. Reproduced from ref 39 with permission from the PCCP Owner Societies.

**Figure 9.** (a) TEM image of IrO$_2$/TiO$_2$. In situ XANES absorption edge of (b) active uncalcined and (c) inactive calcined IrO$_2$/TiO$_2$ at different applied potentials. Reprinted with permission from ref 11. Copyright 2019 American Chemical Society.
Figure 10. Current-voltage curves of electroreduction of OX using a two-electrode system comprising a TiO₂ (JRC-TIO-7) cathode in solution containing OX (0.03 M) and Na₂SO₄ solution (pH 1.0, 40 ml, 0.2 M) and a WO₃ photoanode in Na₂SO₄ solution (pH 5.6, 40 ml, 0.2 M) under light irradiation, with wavelength >200 nm (red), >300 nm (blue) or >400 nm (black), or in the dark (broken line). Reproduced from ref 40 published by The Royal Society of Chemistry.

Figure 11. Schematic image of thermo-electrochemical (TEC) cell that uses pyruvic acid and lactic acid as a redox couple and TiO₂/Ti mesh electrodes (left). Current output and the corresponding power output (right). The dotted curves are inserted a guide.

(Sₑ) of 1.40 mV K⁻¹ (Figure 11). It should be noted that the observed coefficient has a positive sign, although the coefficient calculated from thermodynamic parameters for the redox reaction of lactic acid and pyruvic acid is −2.20 mV K⁻¹. DFT calculations revealed that the positive Sₑ value is ascribed to the small vibration entropy of the pyruvic acid and protons adsorbed on the TiO₂ electrode; this vibration entropy is smaller than that of a free lactic acid molecule, i.e., the formation of a free lactic acid molecule from an adsorbed pyruvic acid preferentially proceeds at higher temperatures. Furthermore, the TiO₂ surface acts as a proton donor (or acceptor) and plays a critical role in determining the polarity of the generated potential. This result indicates that the interaction between redox species and the electrode surface is considerably important in the redox-based TEC conversion systems.41

EHRs combined with the other chemical reactions enable the production of more complicated chemicals than alcohols. Imines or oximes form via the reaction between α-keto acids and ammonia or hydroxylamine. EHRs of mixed solutions of α-keto acids and hydroxylamine achieved the formation of corresponding amino acids with considerably high FE, i.e., high selectivity as shown in Figure 12.42 Furthermore, glycine formation from oxalic acid has also been achieved.43 Recently, DFT calculations have predicted that proton coupled electron transfer (PCET), which couples with the oxide surface and substrate plays a significant role.44 Research on EHRs on oxide electrodes has just begun, and further efforts will identify ideal catalytic surfaces for environments that lead to more efficient EHRs.

Figure 12. Faradaic efficiency for amino acid production via EHRs of corresponding oximes produced from α-keto acids with hydroxylamine. Reproduced from ref 42 with permission from the Chem. Comm. Owner Societies.

Conclusion

To break away from fossil resources and to produce materials from ubiquitous resources using renewable energies, new catalytic functionalities are distinct from those of the past are required. Novel AS catalysts can be used under milder conditions, making them preferable to conventional H-B catalysts, and are expected to produce a carrier for green hydrogen. Hori’s discovery and the rapid progress of theoretical understanding have greatly advanced the development of CO₂ EHR catalysts. We discussed the fundamental functions of alloying. Alloying controls the electronic states and elemental arrangement of metal catalysts and can favorably adjust the interaction strength between a reactant (or an intermediate) molecule and the catalyst surface and hence modify the reaction pathway. If the facet on NAs is precisely controlled, their catalytic selectivity and activity will be further enhanced.

TiO₂ based oxide particles are a new type of EHR catalyst that exhibit highly selective material production. Liquid energy carriers such as GC are selectively produced on anatase TiO₂ paritcles from OX. This review discusses how the energy states and activities of TiO₂ are modified by these influential factors, i.e., the catalytic performance on TiO₂ catalysts is controllable by their morphology and composition. Recently, continuous GC production with a flow type has been achieved; this advancement will be applicable for the energy storage of surplus renewable electricity. Furthermore, applications based on EHRs, such as photoelectrochemical hydrogenation, TEC and the amino acid production have been demonstrated. Both the fundamental understanding and intensive application of nano-catalysts bring us closer to the realization of a sustainable society.
The review was produced with the support of the grant of Joint Research by the National Institutes of Natural Sciences (NINS) (NINS program No. 01112104).

References and Notes