UC Berkeley
UC Berkeley Previously Published Works

Title
Application of Single-Site Catalysts in the Hydrogen Economy

Permalink
https://escholarship.org/uc/item/46t2b8kz

Journal
Trends in Chemistry, 2(12)

ISSN
2589-7209

Authors
Chen, Luning
Qi, Zhiyuan
Zhang, Shuchen
et al.

Publication Date
2020-12-01

DOI
10.1016/j.trechm.2020.09.009

Peer reviewed

Application of Single-Site Catalyst in Hydrogen Economy

Luning Chen,[1,†] Zhiyuan Qi,[1,†] Shuchen Zhang,[1] Ji Su,[1,2,*] Gabor A. Somorjai[1,3,*]

1 Materials Sciences Division, 2 Molecular Foundry, Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States.

3 Department of Chemistry, University of California-Berkeley, Berkeley, California 94720, United States.

† These authors contributed equally to this work.

Correspondence: jisu@lbl.gov (Ji Su); somorjai@berkeley.edu (Gabor A. Somorjai)

Abstract: Catalyst development is a process of evolution. The new generation of single metal sites catalysts, with isolated single metal atoms dispersed among the substrates, offering maximum atom-utilization efficiency (100 %), high specific activity and unique property, thereby bridging the gap between homogeneous catalysts and heterogeneous catalysts. The field is at an early stage, characterized by numerous discoveries and novel demonstration of catalytic properties associated with the fine structure of single metal sites, but specific applications are still lacking. Based on our studies on hydrogen generation/storage with single metal sites catalyst, this review will focus on summarizing the applications of single site catalyst in hydrogen economy. Hoping this work will inspire more summarization on single sites catalyst development from other applications.

Introduction

Hydrogen (H_2) is regarded as an ideal alternative clean energy source, because of its high mass energy density, and producing only water upon combustion.[1-4] Therefore, hydrogen has been applied in different fields to replace the traditional hydrocarbon energy supply, especially in polymer electrolyte membrane fuel cells (PEMFCs) which leads the world's energy structure shifting from fossil fuel economy toward a much cleaner and more reversible hydrogen economy.[5-7] Hydrogen element is abundant on Earth, it is widely exhibiting in a large number of hydrogen-containing compounds, such as methane, water, alcohols, hydrocarbons. To extract H_2 from these compounds,

numerous catalysts have been developed, including both homogenous and heterogenous catalysts.[8-10]

On the other hand, Zhang and co-workers firstly proposed the concept of single-site catalyst: isolated identical active sites dispersed on the solid surface, via successfully demonstrating single Pt sites anchored on iron oxide support (Pt_1/FeO_x), which opened up a new research frontier in catalysis.[11] Since then, with the unique electronic structure and maximum atom utilization, single-site catalysts have been applied in all catalytic fields.[12] Compared with heterogeneous nanocatalysts or homogeneous molecular catalysts, single-site catalysts offer several advantages. Firstly, single-site catalysts achieve the maximum utilization of atoms in heterogeneous catalysis,[13] which is critical to the practical use of noble metal catalysts. Previous studies of nano-catalysts reveal that undercoordinated metal atoms are actual catalytic active sites. Therefore, the specific activity per metal atom usually increased with the decreasing size of particles as smaller particles contain more low-coordinated sites. In principle, the limit small size for catalytic particles, is single-site, which resulted in excellent catalytic performance of single-site catalysts.[14,15] Secondly, single-site catalysts with definite structures provide an ideal model for investigation of reaction fundamentals.[16,17] Each active site of single-site catalysts is structurally well-characterized, spatially isolated, and therefore has the identical interaction with the reactants. Moreover, the interaction between single atom sites and their neighboring coordinated atoms will greatly alter the electronic properties and thus catalytic activity of single-site catalysts, which is similar to the molecular defined organometallic catalysts. Therefore, the single-site catalysts offer a connection between homogeneous catalysis and heterogeneous catalysis.[18-20] Thirdly, the prospects for large-scale application have motivated academic and industrial efforts on the scale-up of single metal sites catalysts synthesis, with Ding Ma group having played a leading role by developing large-scale syntheses to kg level.[21,22] Thus, these achievements provide the potential for cost-effective mass production of single metal sites catalysts and subsequently may open a window for their industrial application.

With its unique electronic properties and structure, as well as exceptional catalytic

performance, the single-site catalyst has been widely tested in different catalytic field. Numerous discoveries and novel demonstration of catalytic properties associated with the fine structure of single metal sites had been found and well-summarized,[23-24] but applications are still lacking. Especially, the summarization of specific direction of application are rare. This review will focus on summarizing the applications of single site catalyst in hydrogen economy. Hoping this work will inspire more summarization on single sites catalyst development from others application direction. And finally place the studies in perspective and point out the research opportunities.

In this short review, we will first summarize the state of art works on the application of single-site catalysts in hydrogen evolution reaction from different hydrogen-rich molecules (i.e. water, methane, methanol) (Figure 1). The advantages and disadvantages of single metal sites catalysts will be discussed. Then, a short outlook will be given on the existing problems with feasible solutions and the potential opportunities.
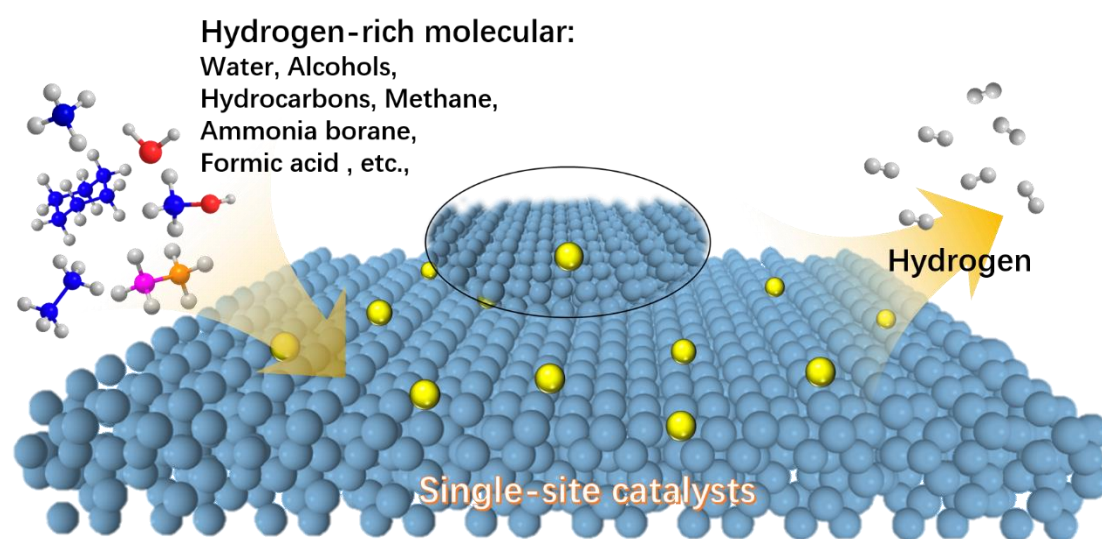

Figure 1. Hydrogen production form different hydrogen-rich molecular on single-site catalysts.

Hydrogen evolution from water

Water is the main constituent of Earth's hydrosphere, covering 71% of Earth's surface. As a hydrogen contained molecular, water could potentially be the most abundant hydrogen source by breaking the strong bond between oxygen and

hydrogen.[25,26] To release hydrogen from water, several reactions have been applied in industry including steam reforming, water gas shift (WGS), water gas reaction.

Among all the reaction generating hydrogen from water, water gas shift (WGS, $CO+H_2O \rightarrow CO_2+H_2$) accounts for an important proportion in hydrogen production while remove carbon monoxide in various energy-related chemical processes.[27] Since its first discovery by Fontana in 1780, a number of experimental and theoretical studies have been devoted to improving the catalytic efficiency and thus reducing the cost of hydrogen produced via WGS. The traditional WGS catalysts are Cu-based. However, the poor activity and the low tolerance to the air and condensed water limited the practical application of Cu catalysts.[28,29] On the other hand, noble metal catalysts supported by reductive metal oxide supports (e.g., CeO_2 or FeO_x) are prepared as the new generation of WGS catalysts with relatively high activity and good stability at low temperature.[30,31] Nevertheless, the high cost of noble metal catalysts hinders their further application. To improve the atomic utilization of precious metals, a variety of single-site catalysts were prepared for the hydrogen production.[32,33] Zhang, Liu, Li and co-workers successfully synthesized a single sites iridium catalysts supported by iron oxide (Ir_1/FeO_x) with 0.01 wt % iridium via a coprecipitation method.[34] This single-site catalyst showed a high specific reaction rate up to 43.4 $mol_{CO} g_{Ir}^{-1} h^{-1}$ at 300 $^{\circ}C$, corresponding to a turnover frequency (TOF) of 2.31 s^{-1}, which is 2-3 times of other reported Ir catalysts and even higher than most active Pt and Au catalysts. Furthermore, they combined the theoretical and experimental study to identify the active sites and clarify the reaction mechanism of WGS on Ir_1/FeO_x single-site catalyst.[35] The authors claimed that the synergistic interaction of Ir_1 and neighboring Fe species reveals a new reaction mechanism with the involvement of O-vacancy, which is different from the conventional associative mechanism involving the formation of formate or carboxyl intermediates. Specifically, the water molecule easily dissociates to OH* on Ir single site and H* on the nearby O atom bonded with Fe. On the other hand, the CO absorbed on Ir site reacted with the adjacent O to produce CO_2, which create an O-vacancy. Finally, two H* coupled together and generated a H_2.

Hydrogen evolution from methane

Expect for water molecule, methane (CH_4), consisting of one carbon atom and four hydrogen atoms, is regarded as another alternative hydrogen resource. Steam methane reforming (SMR) followed by the WGS reaction is the most common process for large-scale hydrogen production in industry. However, the high capital costs and high energy consumption of endothermic SMR process are unavoidable.[36] Alternatively, H_2 can be produced by the direct methane decomposition ($CH_4(g) \rightarrow C(s) + 2H_2(g)$) to yield hydrogen and solid carbon with no CO_2 releasing. Although the production of H_2 is only half compared to SMR, this process needs less energy input while solid carbon could be value-added products..[37] McFarland, Metiu and co-workers applied molten metals, consisting of 27% nickel (Ni) and 73% bismuth (Bi), achieved 95% methane conversion at 1065 °C in a 1.1-meter bubble column and produced pure hydrogen without CO_2 or other by-products (Figure 2).[38] Further calculation proves that the active nickel element is atomically dispersed in the molten alloys with negative charges, leading the enhancement of catalytic activity and stability.
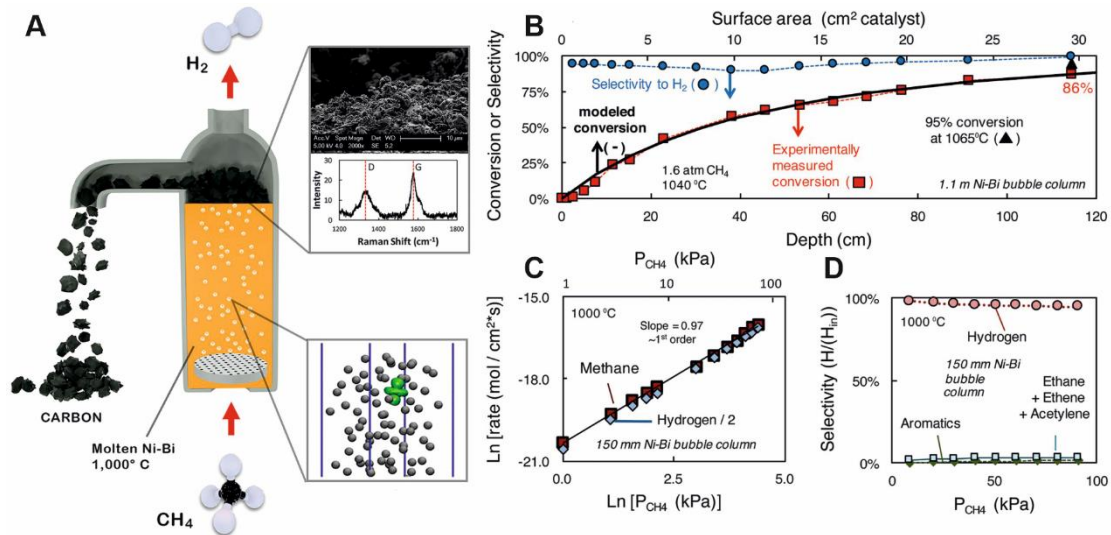

Figure 2. (A) reaction schematic of hydrogen production with a Ni-Bi molten catalyst and reactivity in bubble column: (B) methane conversion and selectivity to hydrogen as a function of inlet-tube depth, (C) logarithm of rate of CH_4 conversion an H_2 yield as a function of logarithm of pressure, (D) selectivity for pyrolysis at 1000 °C as a function of CH_4 partial pressure in argon. Reproduced and adapted, with permission, from [38].

Besides the direct decomposition, the dry reforming of methane (DRM, $CO_2+CH_4 \rightarrow 2CO+2H_2$), converting methane and carbon dioxide into synthesis gas is another world-scale industrial process to generate hydrogen from methane accompanying with mitigation of greenhouse gases, both CO_2 and CH_4.[39] According to intensive studies, Ni-based catalysts were regarded as the most promising material for DRM due to the low cost and high activity. However, the *in situ* catalyst deactivation by coking and sintering of Ni species limited its further commercial application.[40] To prevent the carbon deposition, Qiao and Zhang group reported a single-site Ni catalyst for DRM, in which the isolated Ni atoms are stabilized through the interaction with Ce-doped hydroxyapatite.[41] Unlike Ni nanoparticles, the isolated Ni site performed a unique ability to only activate the first C-H bond of CH_4 molecule, avoiding the further decomposition of methane into carbon due to its unique electronic structure. Moreover, the strong metal-support interaction between the Ce doped hydroxyapatite and single Ni site prevents the aggregation of Ni. Thus, single Ni site catalyst performed high activity and stability for 100 h DRM reaction without carbon deposition and Ni sintering, which offered a low-cost route to commercial dry reforming of methane.

Another way to avoid catalyst deactivation by coking is to decrease the reaction temperature of DRM. Hu, Tao and co-workers successfully anchored two sets of single sites (Ru_1 and Ni_1) on the surface of CeO_2 nanorods, $Ce_{0.95}Ni_{0.025}Ru_{0.025}O_2$ catalyst, which is highly active for DRM at 560 ^{o}C with a turnover rate of 73.6 mol$_{H2}$ mol $_{Pt}^{-1}$ s^{-1}.[42] In addition, $Ce_{0.95}Ni_{0.025}Ru_{0.025}O_2$ performed lower apparent activation barrier and higher turnover rate than monometallic single-site catalyst with only Ni($Ce_{0.95}Ni_{0.05}O_2$) or only Ru ($Ce_{0.95}Ru_{0.05}O_2$), demonstrating the strong synergistic effects of Ru and Ni sites, which is further investigated by the DFT calculations. Ru single sites are believed to dissociate CO_2 to CO while Ni single sites activate CH_4 to form CO. Sequentially, the formed H atom through activation of CH_4 on Ni sites will couple with another H atom to form H_2 on Ru site. Apart from introducing second element to construct dual single-site catalyst, Carter, Nordlander, Halas and co-workers designed a plasmonic photocatalyst consisting of a Cu nanoparticle 'antenna' with single Ru site 'reactor' for light-driven methane dry reforming, which also lowers the reaction temperature.[43] The

calculations showed that the isolated Ru single site on the Cu surface are the optimal active site for DRM because of the lower activation barrier of CH_4 dehydrogenation compared to pristine Cu nanoparticles. Strikingly, the generated hot carrier provided a new photocatalytic DRM mechanism different from the thermally driven reaction. The rate of C-H activation on Ru sites and desorption of H_2 form catalytic surface was enhanced by the hot carriers, enabling the kinetic match of the formation rate of CO and H_2, minimizing the rate of reverse water gas shift (RWGS) and coking reaction.

Hydrogen evolution from light alkanes

Besides methane, dehydrogenation of light alkanes (ethane, propane and butane) to the corresponding light olefins is another potential approach to generate hydrogen, companying with the production of high-value chemicals, which could be the feedstock of various chemicals, including polymers (polyethylene and polypropylene), oxygenates (ethylene glycol, acetaldehyde, acetone, and propylene oxide) and important chemical intermediates (ethylbenzene and propionaldehyde). There are mainly two types of catalysts for light alkane dehydrogenation reaction: noble metal-based (e.g., Pt, Pd, or Ni) and metal oxide-based (e.g., chromium oxide, vanadium oxide, molybdenum oxide or gallium oxide).[44] However, the reaction is highly endothermic and thermodynamically limited. Therefore, higher reaction temperature and lower paraffin partial pressure are needed to achieve high conversion according to Le Chatelier's principle. Indeed, to obtain more than 50% C_2-C_4 alkane conversion at 1 bar, the required reaction temperature is always up to 550 to 750 $^{\circ}$C. Hence, it is still challenging to select suitable catalysts for alkane dehydrogenation at lower temperature with high conversion and good stability.[45]

Shimizu group successfully fabricated isolated indium (In) hydride sites in chabazite (CHA) catalyst by annealing an In-exchanged CHA zeolite (In-CHA) under H_2 at high temperature.[46] Kinetic and *in situ* spectroscopic studies combined with transition state (TS) calculations confirms the isolated $[InH_2]^+$ ion on a framework anionic site served as the catalytic active sites for ethane dehydrogenation via both concerted and alkyl mechanisms (Figure 3). $[InH_2]^+$ sites reduced the abundance of zeolite-coordinated protons and/or carbenium species, leading to much less coke

formation than zeolites exchanged with other element (e.g. Ga-CHA). Therefore, the single-site In-CHA catalyst performed high selectivity and durable catalytic activity for ethane dehydrogenation reaction for at least 90 h.
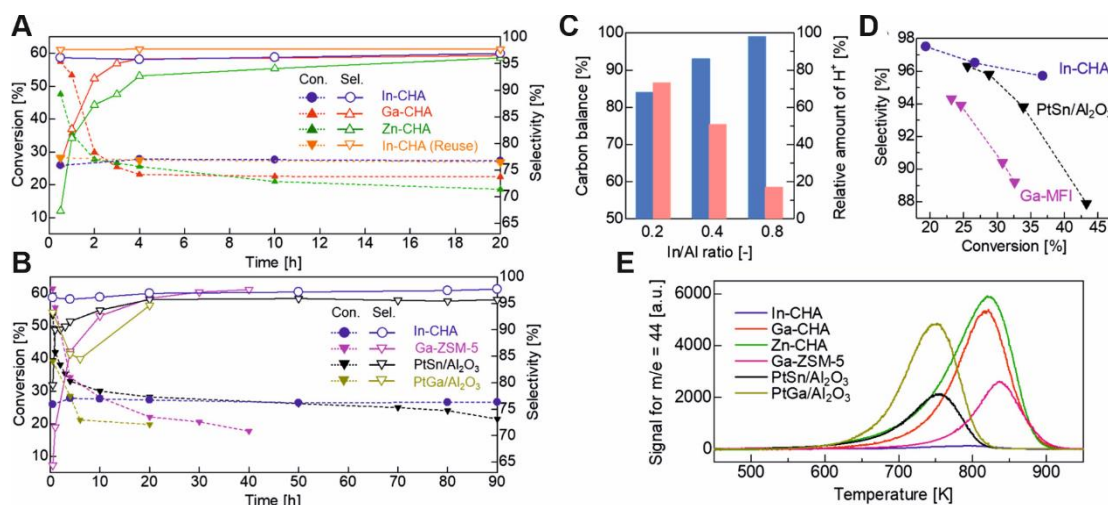

Figure 3. Time course of ethane dehydrogenation using (A) In-, Ga-, and Zn-CHA for 20 h and (B) In-CHA, Al$_2$O$_3$-supported PtSn catalyst (PtSn/Al$_2$O$_3$) for 90 h, PtGa/Al$_2$O$_3$ for 20 h, and Ga-ZSM-5 for 40 h. (C) Effect of In/Al ratio on the carbon balance (blue) and relative amount of Brønsted acid sites normalized to the H-CHA (red). (D) Relationship between conversion and selectivity for In-CHA, PtSn/Al$_2$O$_3$, and Ga-ZSM-5. (E) TPO spectra of the catalysts used for 2 h reaction. Reproduced and adapted, with permission, from [46].

Besides, the single-site catalysts were employed in propane dehydrogenation to improve the catalytic selectivity and stability and lower the reaction temperature.[47,48] Guo group synthesized the γ-alumina-supported platinum/copper single-site catalyst with a high copper to platinum ratio, in which isolated Pt sites were dispersed on Cu nanoparticle via the incipient wetness co-impregnation method with a high copper to platinum ratio.[49] Different from conventional Pt alloy, single-site PtCu catalyst displayed a quite negative difference between the desorption energy and further dehydrogenation barrier of propylene while maintaining a reasonable energy barrier of propane dehydrogenation. Therefore, the novel single-site catalyst performed propylene selectivity of ~90% with high reaction rate of 10.6 mol g$_{pt}^{-1}$h^{-1} and excellent stability for at least 120 h on steam at 520 °C and ambient pressure with a weight hourly space velocity (WHSV) of 4 h^{-1} (propane:N$_2$ =1:1). Butane dehydrogenation reaction

is also an important reaction converting the light, low-value alkanes into high-value chemicals. Wasserscheid group employed gallium-rich Pd-Ga phase as supported liquid metal catalyst, in which single Pd active sites dispersed at the surface of liquid metal for butane dehydrogenation.[50] Compared with previous butane dehydrogenation catalyst, this supported catalyst with an active liquid metal solution performed excellent catalytic activity and stability without coke formation even with pure butane feedstock.

Hydrogen evolution from liquid organic hydrogen carriers (LOCHs)

Till now, the hydrogen storage and transportation approaches include compressed gas and solid-state storage in metal hydrides or metal-organic frameworks (MOFs).[51, 52] However, the practical hydrogen storage and transportation still have challenges due to the low volumetric energy density of hydrogen. The application of small hydrogen-containing molecules as carriers to transport hydrogen in liquid or solid state and generate hydrogen in situ by breaking chemicals bonds, provides a new solution to the above-mentioned problems.[53, 54] Among all the candidates, methanol is an ideal liquid organic hydrogen carrier (LOHC) thanks to its high hydrogen weight percent, low cost and abundant resources.[55] In order to lower the reaction temperature and maximize the Pt atom-utilization efficiency, our group synthesized a single-site Pt_1/CeO_2 catalyst with Pt atoms anchored on the porous CeO_2 by a modified ascorbic acid (AA)-assisted reduction method.[56] Compared with CeO_2 supported Pt nanoparticles with two different sizes (2.5 nm Pt/CeO_2 and 7.0 nm Pt/CeO_2), the single site Pt in Pt_1/CeO_2 is more oxidized, of which the binding energy of Pt-CO is much lower than metallic Pt species on Pt nanoparticles (Figure 4). Thus, the formed CO is much easier to desorb from the positive Pt sites of single-site catalyst during methanol dehydrogenation and release the active sites. Therefore, at a relatively lower temperature, the single-site Pt_1/CeO_2 catalyst displayed excellent hydrogen generation efficiency, 40 times higher than 2.5 nm Pt/CeO_2 catalyst and 800 times higher compared to 7.0 nm Pt/CeO_2 catalyst (Figure 2). Meanwhile, Ma group synthesized an isolated platinum (Pt) sites dispersed on α-molybdenum carbide (α-MoC) catalyst, performed 18046 h^{-1} TOF in aqueous-phase reforming of methanol (APRM) at low-temperature (150-190 ℃).[57] XPS results and DFT calculation further confirmed that the special geometric and electronic

properties resulting from the strong interaction between platinum and α-MoC benefited the APRM reaction. And compared with other APRM catalysts, the synergistic effect between single-site Pt and α-MoC played an important role to improve its catalytic efficiency. Specifically, the α-MoC provided highly active sites for water dissociation producing abundant surface hydroxyls and thus accelerating the methanol-reforming reaction at the interface between Pt_1 and α-MoC.
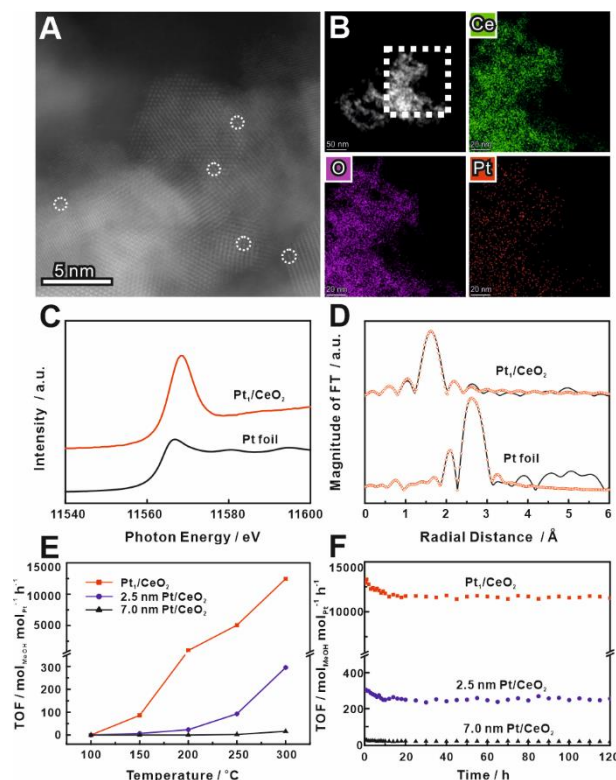

Figure 4. (A) Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and (B) corresponding elemental mappings images of Pt_1/CeO_2 catalyst. (C) normalized XANES spectra and (D) k^3-weighted Fourier transform EXAFS spectra and of Pt_1/CeO_2 and bulk Pt foil at the Pt L_3-edge. (E) (F) the catalytic activity and stability of Pt_1/CeO_2, 2.5 nm Pt/CeO_2 and 7.0 nm Pt/CeO_2. Reproduced and adapted, with permission, from [56].

On the other side, some hydrogen-rich cycloalkanes, like cyclohexane, methylcyclohexane, decalin, perhydro-N-ethylcarbazole, are also regarded as ideal liquid organic hydrogen carriers.[58,59] Moreover, different from methanol of which dehydrogenated product (i.e., CO_2 or CO) directly exhausted to atmosphere, the dehydrogenated products of cycloalkanes are still liquid organic molecules, which are

easily collected and re-hydrogenated back to the corresponding hydrogen-rich cycloalkanes.[60] A model catalyst of graphene-supported nickel single-site for cycloalkane dehydrogenation reaction has been simulated. The calculation results suggest that the dehydrogenation occurs via a C-H insertion followed by β-hydride elimination.[61]

Hydrogen evolution from solid hydrogen contained molecules

Beside the liquid organic molecules, some solid hydrogen-containing molecules also have been employed to the hydrogen storage and transformation. Ammonia-borane (NH_3BH_3, AB) is considered as one of the most outstanding candidates for chemical H_2 storage and production owing to its high hydrogen content, non-toxicity, and superior stability in aqueous solutions.[62-65] Apart from the traditional supported metallic catalysts, single-site catalysts on different substrates have been employed for H_2 generation *via* AB hydrolysis reaction.[66] For instant, a single-atom alloy made of atomically dispersed Pt single-site on the surface of Ni particles were employed in hydrolytic dehydrogenation of ammonia-borane reaction. With the synergistic effect between Pt and Ni where the negatively charged Pt ($Pt^{\delta-}$) and positively charged Ni ($Ni^{\delta+}$) promote the interact with H and OH, this Pt single-site catalyst performed enhanced catalytic activity of 12000 mol_{H2} mol_{Pt}^{-1} min^{-1} which is 21 times of the best Pt-based catalyst ever reported.[67] Apart from single active site anchored on metal support, the metal oxides are also employed as supports to isolate active sites, which provides another approach to adjust the electronic structure and catalytic performance of the single active sites.[68] Lu and co-workers applied atomic layer deposition (ALD) method to fabricate a series of Pt single-site catalysts with different supports including Co_3O_4, CeO_2, ZrO_2 and graphene.[69] Variation of the supports is an effective way to tailor the strong electronic metal-support interactions (EMSIs), which gave rise to the various 5d electronic states of single-site Pt. The authors claimed the strong EMSIs exhibited in Pt_1/Co_3O_4, leading to a lager depletion of 5d states of Pt atoms compared to other catalysts, which modulated the adsorption of AB and assisted the hydrogen desorption. Therefore, the single-site Pt_1/Co_3O_4 catalysts performed the boosted

activity up to 68-fold higher as well as excellent stability comparing with single-site Pt loaded on other supports or nanoparticle catalysts.
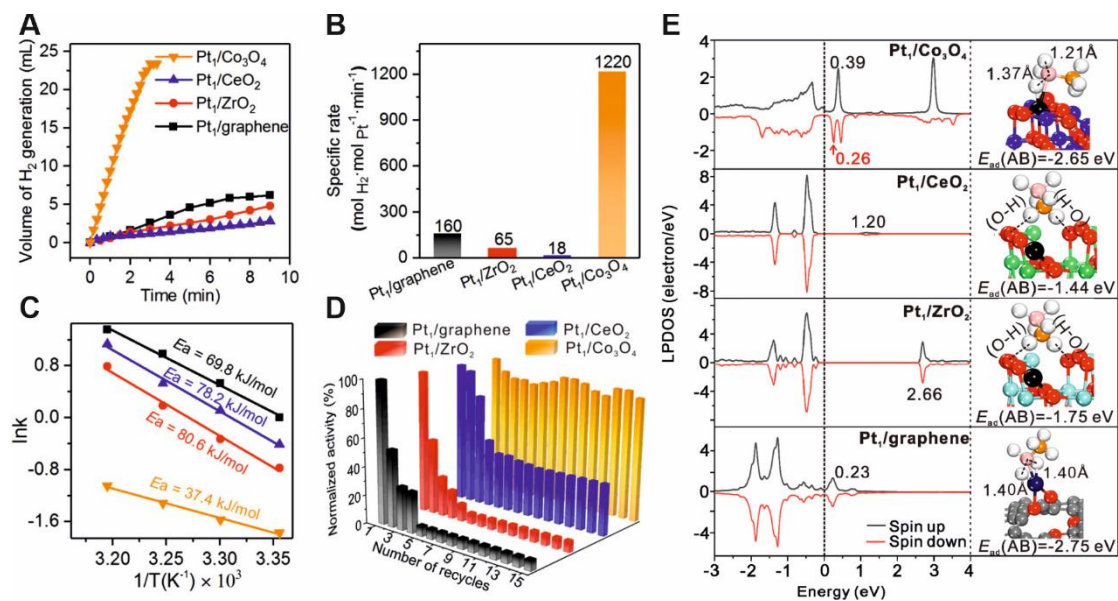

Figure 5. Catalytic performance of Pt_1 single-site catalysts in hydrolytic dehydrogenation of AB at 25 °C. (A) Plots of the volume of H_2 generated as a function of time, (B) mass specific rates, (C) Arrhenius plots, and (D) recyclability test on Pt_1/Co_3O_4, Pt_1/CeO_2, Pt_1/ZrO_2, and $Pt_1/graphene$ single-site catalysts. (E) Local partial density of state (LPDOS) projected on the Pt_1 5d orbitals with the Fermi level set at zero and the local configurations for AB adsorption. Reproduced and adapted, with permission, from [69].

Furthermore, formic acid, which produces CO_2 and H_2 via dehydrogenation on metal surface, is regarded as an alternate for hydrogen generation and storage.[70-72] Sykes group studied the formic acid dehydrogenation on single-atom alloys,[73] which comprise catalytically active elements like Pt, Pd and Ni alloyed in more inert host metals at the single-atom limit.[74] They successfully substituted the single-site Pt into the Cu lattices to form the PtCu single-site catalyst. And surface mechanism indicated that SAAs did not increase of formic acid dehydrogenation but significantly decresed energy barriers for O-H bond breaking which holds promise for other dehydrogenation reaction. Therefore, the PtCu single-site catalyst is able to selectively dehydrogenate formic acid with 6-fold increase yield in comparison to Cu. Moreover, noble metal single site dispersed on N-doped carbon material is also an important type of single-

site catalyst applying in the formic acid dehydrogenation.[75] Bulusheva group reported a Pd single-site catalyst supported by nitrogen-functionalized mesoporous carbon, which significantly enhanced the catalytic decomposition of vapor-phase formic acid for hydrogen production, providing an increase by 2-3 times in comparison to supported Pd nanoparticle catalysts.[76] Further density functional theory (DFT) calculation indicated that the isolated Pd atom is the active site for formic acid decomposition into absorbed hydrogen atom and a carboxyl fragment. Interestingly, only the Pd atoms, which is coordinated by a pair of pyridinic-type nitrogen located on open edge of graphene performed catalytic activity. Expect for some noble metal, single transition metal site anchored on nitrogen-doped carbon catalysts can be as well employed in formic acid dehydrogenation. For instance, Beller and co-workers synthesized Co-N-C catalysts with single cobalt sites by pyrolysis of zeolitic imidazolate frameworks (ZIFs). And in the dehydrogenation of formic acid, the single-site Co-N-C catalysts with high reactivity and acidic resistance performed excellent catalytic activities and stabilities compared with Co nanoparticle catalysts.[77]

Concluding Remarks

As an attractive alternative energy carrier, hydrogen has been significantly applied in different fields including polymer electrolyte membrane fuel cells, fine chemical synthesis and traditional chemical industry like ammonia synthesis, Fischer-Tropsch reaction, etc. The increasing demand of hydrogen requires the design of novel, efficient and stable catalysts for hydrogen generation, among which the single-site catalysts might bring in unique insights and open up more possibilities of catalyst design and construction for hydrogen production.

However, to employ single-site catalysts in practical application there are still some challenges need to overcome. Firstly, till now the single-site catalyst has been widely applied in small molecule catalyst, like CO oxidation, hydrogenation and so on. However, the lack of an ensemble of active atoms adjacent to the single noble metal atom in most of these single site catalysts prevents surface reactions that involve large molecules.[78] Second, although single-site catalysts performed outstanding catalytic activity and selectivity in some reaction. There are few studies focused on the structure-

function relationship of single-site catalysts, especially the functional of supports during catalytic process. To design suitable single-site catalyst for a specific hydrogen generation reaction. It is vital to make a deep understanding of mechanism for single-site catalysis.

Moreover, although there are some reports about the efficient single-site catalysts in hydrogenation generation reaction from small molecular dehydrogenation process. For most examples, after hydrogen release, the leaving by-product are also gases like CO, CO_2 which are always hard to be collected and re-hydrogenated back to hydrogen contained molecule. So, there is still need to seek a system of which the dehydrogenated product is also liquid and can be re-hydrogenated to original molecule to achieve the reversable hydrogen storage and transportation, like systems of cyclohexane/benzene and methylcyclohexane/toluene. Besides, for the material research, there are still need to seek for a bifunctional single-site catalyst, which not only performed high activity in dehydrogenation reaction, but also can be applied in the re-hydrogenation of corresponding hydrogen-lean molecule.

In conclusion, we summarized the state-of-the-art applications of single site catalyst in hydrogen generation form different hydrogen sources, such as water, methane, light alkanes, liquid organic hydrogen carriers (LOCHs) as well as solid hydrogen carriers. Compared to the traditional metal nano-particles catalyst, the single metal site catalysts show significantly advantages on catalytic efficiency, product selectivity, as well as providing an ideal platform to study the structural-functional relationship. With the demand for hydrogen anticipated to reach 122.5 M tons in 2024, new and improved catalysts materials and reaction processes are required to drive innovation for the development of a highly efficient, stable and low-cost hydrogen generation/storage process. Therefore, with the continuous development of single-site catalyst materials, it is possible to design the practical, efficient, and stable catalysts for hydrogen economy.

Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Muradov, N. Z. *et al.* (2005) From hydrocarbon to hydrogen-carbon to hydrogen economy. *Int. J. Hydrog. Energy*, 30, 225-237.

2. Muradov, N. Z. *et al.* (2008) "Green" path from fossil-based to hydrogen economy: an overview of carbon-neutral technologies. *Int. J. Hydrog. Energy*, 33, 6804-6839.

3. Goltsov, V. A. *et al.* (2001) From hydrogen economy to hydrogen civilization. *Int. J. Hydrog. Energy* 26, 909-915.

4. Tromp, T. K. *et al.* (2003) Potential environmental impact of a hydrogen economy on the stratosphere. *Science* 300, 1740-1742.

5. Schultz, M. G. *et al.* (2003) Air pollution and climate-forcing impacts of a global hydrogen economy. *Science* 302, 624-627.

6. Tseng, P. *et al.* (2005) A hydrogen economy: opportunities and challenges. *Energy* 30, 2703-2720.

7. Steele, B. C. *et al.* (2011) A Materials for fuel-cell technologies. *Nature* 414, 345.

8. Sordakis, K. *et al.* (2018) Homogeneous catalysis for sustainable hydrogen storage in formic acid and alcohols. *Chem. Rev.* 118, 372-433.

9. Koper, M. T. *et al.* (2010) Electrochemical hydrogen production: bridging homogeneous and heterogeneous catalysis. *Angew. Chem. Int. Ed.* 49, 3723-3725.

10. Tanksale, A. *et al.* (2010) A review of catalytic hydrogen production processes from biomass. *Renew. Sust. Energ. Rev.* 14, 166-182.

11. Qiao, B. *et al.* (2011) Single-atom catalysis of CO oxidation using Pt_1/FeOx. *Nat. Chem.* 3, 634.

12. Yang, X. F. *et al.* (2013) Single-atom catalysts: a new frontier in heterogeneous

catalysis. *Acc. Chem. Res.* 46, 1740-1748.

13. Wang, A. *et al.* (2018) Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* 2, 65-81.

14. Kuhn, J. N. *et al.* (2008) Structure sensitivity of carbon-nitrogen ring opening: impact of platinum particle size from below 1 to 5 nm upon pyrrole hydrogenation product selectivity over monodisperse platinum nanoparticles loaded onto mesoporous silica. *J. Am. Chem. Soc.* 130, 14026-14027.

15. Tsung, C. K. *et al.* (2009) Sub-10 nm platinum nanocrystals with size and shape control: catalytic study for ethylene and pyrrole hydrogenation. *J. Am. Chem. Soc.* 131, 5816-5822.

16. Chen, Y. *et al.* (2018) Single-atom catalysts: synthetic strategies and electrochemical applications. *Joule* 2, 1242-1264.

17. Zhang, H. *et al.* (2018) Single- atom catalysts: emerging multifunctional materials in heterogeneous catalysis. *Adv. Energy Mater.* 8, 1701343.

18. Li, X. *et al.* (2019) Catalyst: Single-atom catalysis: directing the way toward the nature of catalysis. *Chem* 5, 2733-2735.

19. Wang, A. *et al.* (2018) Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* 2, 65-81.

20. Jiao, L. *et al.* (2020) When Nanozymes Meet Single-Atom Catalysis. *Angew. Chem. Int. Ed.* 59, 2565-2576

21. He, X. *et al.* (2020) Mechanochemical kilogram-scale synthesis of noble metal single-atom catalysts. *Cell Rep. Phys. Sci.* 1, 100004.

22. Qu, Y. *et al.* (2018) Direct transformation of bulk copper into copper single sites via emitting and trapping of atoms. *Nat. Catal.* 1, 781-786.

23. Liu, L. *et al.* (2018) Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. *Chem. Rev.* 118, 4981−5079.

24. Gates, B. C. (2019) Atomically Dispersed Supported Metal Catalysts: Seeing Is Believing. *Trends in Chemistry* 1, 99−110.

25. Landman, A. *et al.* (2017) Photoelectrochemical water splitting in separate oxygen and hydrogen cells. *Nat. Mater.* 16, 646-651.

26. Zhang, J. *et al.* (2017) Efficient hydrogen production on $MoNi_4$ electrocatalysts with fast water dissociation kinetics. *Nat. Comm.* 8, 1-8.

27. Flytzani-Stephanopoulos, M. (2014) Gold atoms stabilized on various supports catalyze the water-gas shift reaction. *Acc. Chem. Res.* 47, 783-792.

28. Rodriguez, J. A. *et al.* (2007) Water gas shift reaction on Cu and Au nanoparticles supported on CeO2 (111) and ZnO (000-1): intrinsic activity and importance of support interactions. *Angew. Chem. Int. Ed.* 46, 1329-1332.

29. Wang, Y. X. *et al.* (2019) A systematic theoretical study of water gas shift reaction on Cu (111) and Cu (110): Potassium effect. *ACS Catal.* 9, 2261-2274.

30. Yao, S. *et al.* (2017) Atomic-layered Au clusters on α-MoC as catalysts for the low-temperature water-gas shift reaction. *Science* 357, 389-393.

31. Fu, Q. *et al.* (2003) Active nonmetallic Au and Pt species on ceria-based water-gas shift catalysts. *Science* 301, 935-938.

32. Yang, M. *et al.* (2015) A common single-site Pt(II)-O(OH)x-species stabilized by sodium on "active" and "inert" supports catalyzes the water-gas shift reaction. *J. Am. Chem. Soc.* 137, 3470-3473.

33. Yang, M. *et al.* (2017) Design of single-atom metal catalysts on various supports for the low-temperature water-gas shift reaction. *Catal. Today* 298, 216-225.

34. Lin, J. *et al.* (2013) Remarkable performance of Ir_1/FeO_x single-atom catalyst in water gas shift reaction. *J. Am. Chem. Soc.* 135, 15314-15317.

35. Li, J. *et al.* (2020) Dual metal active sites in an $Ir_1/FeOx$ single- atom catalyst: a redox mechanism for the water- gas- shift reaction. *Angew. Chem. Int. Ed.* 10.1002/anie.201914867

36. Bakenne, A. *et al.* (2016) Sankey-Diagram-based insights into the hydrogen economy of today. *Int. J. Hydrogen Energ.* 41, 7744-7753.

37. Van Der Zwet, G. P. *et al.* (1989) Pyrolysis of methane and the role of surface area. *Catal. Today* 4, 365-369.

38. Upham, D. C. *et al.* (2017) Catalytic molten metals for the direct conversion of methane to hydrogen and separable carbon. *Science* 358, 917-921.

39. Pakhare, D. *et al.* (2014) A review of dry (CO_2) reforming of methane over noble

metal catalysts. *Chem. Soc. Rev.* 43, 7813-7837.

40. Shi, L. E. I. *et al.* (2013) An introduction of CO_2 conversion by dry reforming with methane and new route of low-temperature methanol synthesis. *Acc. Chem. Res.* 46, 1838-1847.

41. Akri, M. *et al.* (2019) Atomically dispersed nickel as coke-resistant active sites for methane dry reforming. *Nat. Comm.* 10, 1-10.

42. Tang, Y. *et al.* (2019) Synergy of single-atom Ni_1 and Ru_1 sites on CeO_2 for dry reforming of CH_4. *J. Am. Chem. Soc.* 141, 7283-7293.

43. Zhou, L. *et al.* (2020) Light-driven methane dry reforming with single atomic site antenna-reactor plasmonic photocatalysts. *Nat. Energy* 5, 61-70.

44. Sattler, J. J. *et al.* (2014) Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* 114, 10613-10653.

45. Sinfelt, J. H. (1964) Hydrogenolysis of Ethane over Supported Platinum. *J. Phys. Chem.* 68, 344-346.

46. Maeno, Z. *et al.* (2020) Isolated Indium Hydrides in CHA Zeolites: Speciation and Catalysis for Nonoxidative Dehydrogenation of Ethane. *J. Am. Chem. Soc.* 142, 4820-4832.

47. Schweitzer, N. M. *et al.* (2014) Propylene hydrogenation and propane dehydrogenation by a single-site Zn^{2+} on silica catalyst. *ACS Catal.* 4, 1091-1098.

48. Hu, B. *et al.* (2015) Isolated FeII on silica as a selective propane dehydrogenation catalyst. *ACS Catal.* 5, 3494-3503.

49. Sun, G. *et al.* (2018) Breaking the scaling relationship via thermally stable Pt/Cu single atom alloys for catalytic dehydrogenation. *Nat. Comm.* 9, 1-9.

50. Taccardi, N. *et al.* (2017) Gallium-rich Pd-Ga phases as supported liquid metal catalysts. *Nat. Chem.* 9 862.

51. Züttel, A. (2003) Materials for hydrogen storage. *Mater. Today* 6, 24-33.

52. Jena, P. (2011) Materials for hydrogen storage: past, present, and future. *J. Phys. Chem. Lett.* 2, 206-211.

53. Preuster, P. *et al.* (2017) Liquid organic hydrogen carriers (LOHCs): toward a hydrogen-free hydrogen economy. *Acc. Chem. Res.* 50, 74-85.

54. Markiewicz, M. *et al.* (2015) Environmental and health impact assessment of Liquid Organic Hydrogen Carrier (LOHC) systems-challenges and preliminary results. *Energy Environ. Sci.* 8, 1035-1045.

55. Liu, W. C. *et al.* (2018) The methanol economy: methane and carbon dioxide conversion. *Top. Catal.* 61, 530-541.

56. Chen, L. N. *et al.* (2019) Efficient Hydrogen Production from Methanol Using a Single-Site Pt_1/CeO_2 Catalyst. *J. Am. Chem. Soc.* 141, 17995-17999.

57. Lin, L. *et al.* (2017) Low-temperature hydrogen production from water and methanol using Pt/α-MoC catalysts. *Nature* 544, 80-83.

58. Modisha, P. M. *et al.* (2019) The prospect of hydrogen storage using liquid organic hydrogen carriers. *Energ. Fuel*. 33, 2778-2796.

59. Preuster, P. *et al.* (2017) Liquid organic hydrogen carriers (LOHCs): toward a hydrogen-free hydrogen economy. *Acc. Chem. Res.* 50, 74-85.

60. Modisha, P. M. *et al.* (2019) The prospect of hydrogen storage using liquid organic hydrogen carriers. *Energ. Fuel* 33, 2778-2796.

61. Borrome, M. *et al.* (2019) Gas- Phase Dehydrogenation of Alkanes: C-H Activation by a Graphene- Supported Nickel Single- Atom Catalyst Model. *Angew. Chem. Int. Ed.* 56, 14906-14910.

62. Rossin, A. *et al.* (2016) Ammonia-borane and amine-borane dehydrogenation mediated by complex metal hydrides. *Chem. Rev.* 116, 8848-8872.

63. Keaton, R. J. *et al.* (2007) Base metal catalyzed dehydrogenation of ammonia-borane for chemical hydrogen storage. *J. Am. Chem. Soc.* 129, 1844-1845.

64. Metin, O. *et al.* (2010) Monodisperse nickel nanoparticles and their catalysis in hydrolytic dehydrogenation of ammonia borane. *J. Am. Chem. Soc. 132*, 1468-1469.

65. Zhang, X. *et al.* (2017) Ruthenium-catalyzed ammonia borane dehydrogenation: mechanism and utility. *Acc. Chem. Res.* 50, 86-95.

66. Sun, Q. *et al.* (2019) Zeolite- Encaged Single- Atom Rhodium Catalysts: Highly-Efficient Hydrogen Generation and Shape- Selective Tandem Hydrogenation of Nitroarenes. *Angew. Chem. Int. Ed.* 58, 18570-18576.

67. Li, Z. *et al.* (2017) Atomically dispersed Pt on the surface of Ni particles: synthesis

and catalytic function in hydrogen generation from aqueous ammonia-borane. *ACS Catal.* 7, 6762-6769.

68. Wang, L. *et al.* (2017) Supported rhodium catalysts for ammonia-borane hydrolysis: Dependence of the catalytic activity on the highest occupied state of the single rhodium atoms. *Angew. Chem. Int. Ed.* 56, 4712-4718.

69. Li, J. *et al.* (2019) Highly active and stable metal single-atom catalysts achieved by strong electronic metal-support interactions. *J. Am. Chem. Soc.* 141, 14515-14519.

70. Eppinger, J. *et al.* (2017) Formic acid as a hydrogen energy carrier. *ACS Energy Lett.* 2, 188-195.

71. Li, Z. *et al.* (2017) Metal-nanoparticle-catalyzed hydrogen generation from formic acid. *Acc. Chem. Res.* 50, 1449-1458.

72. Su, J. *et al.* (2015) Highly efficient hydrogen storage system based on ammonium bicarbonate/formate redox equilibrium over palladium nanocatalysts. *ChemSusChem* 8, 813-816.

73. Marcinkowski, M. D. *et al.* (2017) Selective formic acid dehydrogenation on Pt-Cu single-atom alloys. *ACS Catal.* 7, 413-420.

74. Giannakakis, G. *et al.* (2018) Single-atom alloys as a reductionist approach to the rational design of heterogeneous catalysts. *Acc. Chem. Res.* 52, 237-247.

75. Bulushev, D. A. *et al.* (2016) Single atoms of Pt-group metals stabilized by N-doped carbon nanofibers for efficient hydrogen production from formic acid. *ACS Catal.* 6, 3442-3451.

76. Bulushev, D. A. *et al.* (2016) Single isolated Pd^{2+} cations supported on N-doped carbon as active sites for hydrogen production from formic acid decomposition. *ACS Catal.* 6, 681-691.

77. Li, X., *et al.* (2020). Co- based Single Atom Site Catalysts with High Stability for Selective Dehydrogenation of Formic Acid *Angew. Chem. Int. Ed.* 10.1002/anie.202004125.

78. Jeong, H. *et al.* (2020) Highly durable metal ensemble catalysts with full dispersion for automotive applications beyond single-atom catalysts. *Nat. Catal.* 3, 368-375.

Highlight Hydrogen, is regarded as an ideal alternative clean fuel to take place of traditional fossil fuel due to its high mass energy density and wide range resources. However mostly hydrogen is stored in other molecule instead of exhibiting as free hydrogen molecule. Therefore, to meet the hydrogen demand of industry and daily life, it is vital to seek a low-cost and efficient catalyst to produce hydrogen form hydrogen-contained molecule. The appearance of single-site catalysts provides a new approach to solve this problem due to its maximum atom-utilization and unique electronic structure. With the further in-depth study, the single-site catalyst potentially become the next generation materials for hydrogen economy.

How to explore single-site catalysts in large molecules reaction?

What the function of support during the catalytic process of single-site catalysts? How to modify the electronic structure of active site by controlling the local environment around single active sites?

How to identify the structural-functional relationship by some model catalysts and reactions?

How to synthesize a large scale of single-site catalysts? Can single-site catalysts be employed in practical industry application?