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Engineering of electrocatalysts for methanol oxidation reaction: Recent advances and future challenges

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ABSTRACT

The electrochemical methanol oxidation reaction (MOR) has garnered a lot of attention in recent years as a potential driving force behind the advancement of fuel cell technology. Despite this, the MOR process is still quite difficult since it involves numerous extremely slow H^+/e^-steps, which necessitate the use of efficient electrode material. Despite the fact that Pt-based electrodes exhibit good MOR activity, it is not possible to use them with this technology on a large scale because of their low stability, alcohol tolerance, and high price. This review focuses on the fundamentals of the methanol oxidation reaction, together with their influencing factors, and activity descriptors. In addition, the current developments in non-Pt electrocatalysts for MOR applications are also highlighted. In conclusion, we discussed the difficulties that we have encountered with MOR as well as the opportunities that lie ahead.

1. Introduction

With the shift in the energy market towards renewable power, energy storage during peak production and release during intermittency are becoming increasingly important. An extensive study has been conducted on the feasibility of generating chemical fuels from renewable energy sources through the electrochemical reduction of commonly available substances, such as H_2O, and CO_2 [1–4]. However, the other part of this cycle, though, which involves efficiently extracting useful energy from chemical fuels, is frequently disregarded. Despite its inherent inefficiency, combustion remains the most popular method for extracting energy from carbon-based fuels. Hydrogen fuel cells (H_2-FCs) are now on the market, and fuel cell technology has the potential to achieve even greater theoretical efficiencies [1]. An appealing substitute for H_2-FCs is direct methanol fuel cells (DMFCs), which use liquid methanol (CH_3OH) instead of H_2 gas due to their higher volumetric energy density and ease of storage and transportation (Fig. 1) [2]. In principle, CO_2 and H_2O should be the products of DACs to obtain the maximum possible energy. Oxidation of one mole CH_3OH under standard conditions should liberate 6 mol of electrons along with 1 mole of CO_2 at E0 of 0.016 V vs. SHE, as shown in Eq. (1) [3].

$$CH_3OH+H_2 \rightarrow CO_2+6H^++6e^- \quad E^\circ=0.016\text{ V vs SHE} \tag{1}$$

With its large-scale production from syngas (approx. 90 million metric tones/year) and its potential for large-scale production from CO_2 reduction, CH_3OH is an attractive choice for the foundation of a carbon-neutral energy cycle both now and in the future. A complete CH_3OH oxidation to CO_2, involving $6(H^+/e^-)$, is the fundamental concept for its remarkable energy density (Fig. 1) [4]. Although the possible approaches to achieving the quick and energy-efficient multi-steps (involving the H^+/e^- pair) essential for this transformation are poorly understood, the whole electrocatalytic CH_3OH oxidation process is assumed to be extremely sluggish and involve three steps of $2(H^+/e^-)$ transfer, as shown in Scheme 1. To accelerate the reaction kinetics, Pt and Ru-based heterogeneous electrocatalysts were found to be the potential models for an effective CH_3OH oxidation process, with the limitations of remarkable overpotential as well as poor selectivity. During

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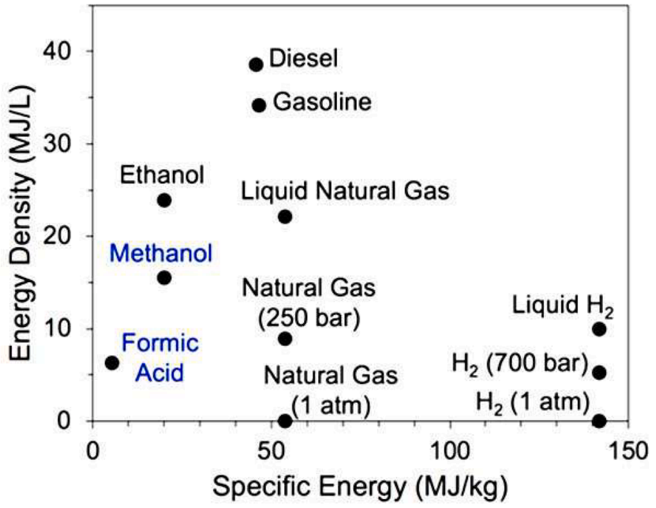

Fig. 1. A systematic illustration of Energy densities of energy-rich chemical molecules. Taken from [4]. Copyright 2019. American Chemical Society.

electro-oxidation, they frequently produce CO, which firmly attaches to the active sites of the catalyst and significantly reduces efficiency [5–9]. In contrast, molecular electrocatalysts based on Ru and Fe have been acknowledged for use in the methanol oxidation reaction (MOR), which prevents the generation of CO during the full oxidation of CH_3OH [10]. Commonly, these chemical systems can produce metal-oxo intermediates, which are potent oxidants that can easily react with CH_3OH by H^+/e^- transfer. However, the practical application of metal-oxo intermediates is limited because their production necessitates a high positive potential [11]. Consequently, more electrochemical oxidants for the transformation of CH_3OH to CO_2 are urgently required. Notwithstanding this necessity, there has been a dearth of reported non-oxo-molecular electrocatalysts for MOR.

By outlining the benefits of molecular electrocatalysts compared to their heterogeneous equivalents, this review hopes to give the most up-to-date information on molecular catalysts for the electrocatalytic MOR process. Moreover, the other MOR electrocatalysts are also briefly discussed, comparing their performance with molecular electrocatalysts. In addition, the article delves into the topic of molecular catalysts and their critical intermediates, exploring how their structure and properties relate to the challenges of achieving faster MOR kinetics and improved selectivity [12]. In addition, we discuss the benefits and drawbacks of each system and offer suggestions for how to improve catalysts for use in DMFCs.

2. Methanol oxidation reaction on catalytic active site

Typically, the MOR process takes place in either an acidic or basic environment. However, the use of an alkaline electrolyte allows for the development of cost-effective and promising electrocatalysts for MOR. Additionally, this approach offers the opportunity to create catalysts that are also suited for ORR for the application of DMFCs [5–7]. The oxidation of CH_3OH in both acidic and basic electrolytes is a six-electron process, as demonstrated in Eqs. (2), (3) [13].

$$CH_3OH+H_2O\rightarrow CO_2+6H^++6e^- \; E^{\circ}=0.02\ \mathrm{V;p^H}=0 \tag{2}$$

$$CH_3OH+6OH^-\rightarrow CO_2+5H_2O+6e^- \; E^{\circ}=-0.81\ \mathrm{V;p^H}=14 \tag{3}$$

In most cases, MOR requires elaborate chemical reactions that generate CO_2 in an indirect manner, involving the formation of intermediates via multiple reaction routes, as seen in Fig. 2(a, b) [14]. As can be seen in Fig. 2a, generally, MOR follows CO pathway (indirectly as

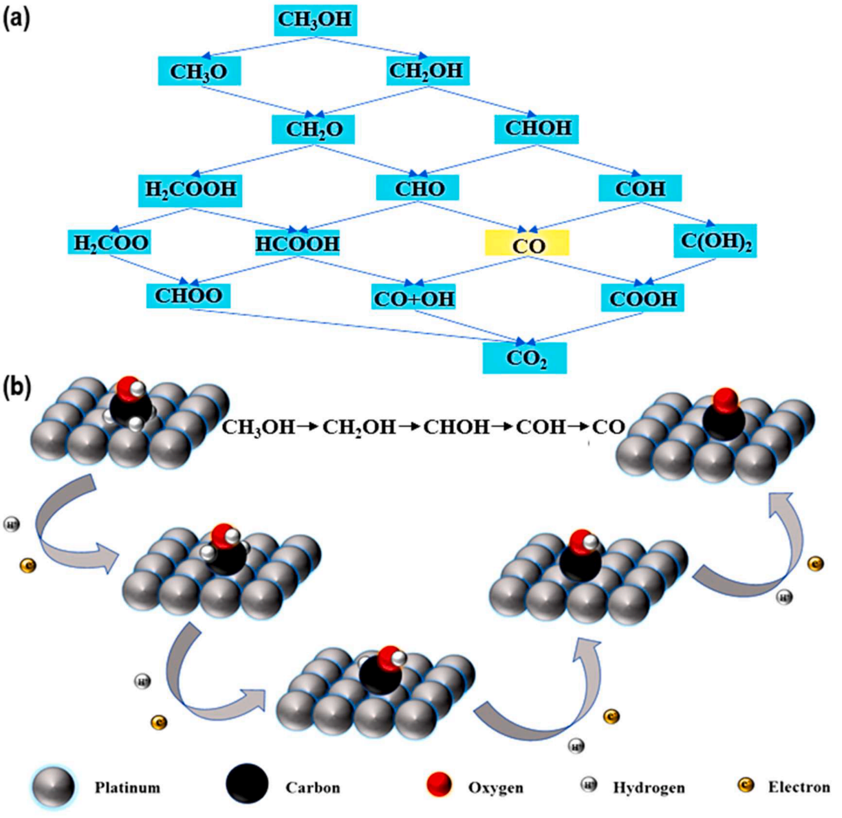

Fig. 2. (a) MOR reaction mechanisms and products, (b) The successive stripping of H^-atoms during MOR. Adapted with permission [14]. Copyright @2022, Taylor & Francis.

well as directly) rather than the 6e- protocol. Adsorption of CH_3OH on the catalyst surface is the first step in MOR, followed by dehydrogenation, rupturing the C—H bond, and/or dehydrogenation to form adsorbed methoxy (CH_3O) [15] via the disposal of acidic hydrogen. Rupturing of the C—H bond makes hydroxy-methyl $(CH_2O)_{ads}$ and ultimately CO_{ads} in indirect protocol [16,17]. The O—H bond breaking can create $(CH_3O)_{ads}$ and formaldehyde due to its dehydrogenation to get desorbed to solution and/or deoxidized again. CO and formate are considered stable intermediates of MOR on Pt, which is likely to affect the efficiency and kinetics of MOR.

Particularly, due to the high stability of CO at low potential at 25–75 °C (usually formed on the heterogeneous catalyst's surface), it not only hampers the MOR kinetics but also initiates poor performance by blocking the catalytic active sites of the electrocatalysts [18]. However, due to the fact that CO can be removed from the catalyst's active sites by compelling its oxidation with H2O or OH-ions, the concerned scientific community incorporated the single atomic Pt sites with other transition metals buried in carbon-based support to boost catalytic performance and protect against CO poisoning [19]. For instance, incorporation of Pt with Ru (a Pt-Ru bimetallic alloy catalyst) significantly improved the catalytic MOR activity [20]. The poisoning effect of intermediates could be determined by catalyst loading, electrolyte flow, and temperature. The following section provides a systematic discussion of the latest developments in catalysts for the MOR process, including those based on noble metals, non-noble metals, and molecular systems.

3. Recent advancements in electrocatalysts for methanol oxidation reaction

3.1. Nobel metal-based catalysts

Experimental studies revealed the dependence of PGM based catalyst for their catalytic activities on alcohol fuel. For instance, oxidation rate of various alcohol electrochemically in alkaline environment on a Pd electrode increased in the order of methanol greater than methanol> glycerol> ethylene glycol> ethanol> isopropanol> *n*-propanol. On the contrary, a different order was found on Pt electrode; methanol> *n*-propanol> ethylene glycol> glycerol> ethanol> isopropanol [21]. Adsorption energy is poorly related to the d-band centres of metals [22]. A strong bonding appears on shifting up of the d-band center with distinctive antibonding above fermi-level. While down-shifting of the d-band center creates the appearance of weak bonding [23]. However, the shifting of the d-band center reflects the change in electron density around the core metal [24]. The design of electrocatalysts with modified electronic structures that have superior electrocatalytic activity has been fabricated using this theory [25]. For example, due to a difference in electronegativity, Sn contributes electrons to Pt, resulting in the down-shifting of the d-band center of the Pt with chemo-sorption energy with CO-intermediate on the Pt-Sn electrocatalyst. Similarly, Co and Ni bring down the shifting of the d-band center of Pt and thus bring down chemisorption energy with OH species and make more active sites for ORR, MOR, and EOR on Pt-Co and Pt-Ni electrocatalysts [26]. It is reported that N-dopant offers electrons to the carbon lattice to promote fermi level, and charge transfer rate gets enhanced in ORR [27]. In this context, Pt-Rh NPs-assisted tungsten nitride decorated on the surface of CNTs displayed superior catalytic performance with better CO poisoning tolerance for EOR due to the synergistic effect of tungsten nitride along with the N-doping effect on CNTs [28]. Charge functional groups anchoring on CNTs may affect the change step of the loading catalyst, which ultimately affects catalytic activity by such a type of electrocatalyst. For instance, Wang et al. [29] demonstrated the effect of assembled polyelectrolytes (PEs) on the surface of CNTs on the electrocatalytic activity and charge transfer process of supported Pt NPs (Fig. 3(a, b)).

Theoretical and experimental results suggest the charged functional group of Pes to have effect on d-band center to alter electrocatalytic activity of Pt NPs. The negatively charged functional group of polyanions like poly-styrene sulphonic acid (PSS)and polyacrylic acid (PAA) made the down shifting of d-band center of Pt NPs to enhance catalytic activity of Pt NPs for MOR. At the same time, Pt NPs with polycations (polydiallydimethyl-ammonium chloride), PDDA, and (polyallylamine hydrochloride), PAH displays up-shifting of d-band center causing reduction of catalytic activity towards MOR [30–32].

Since the geometric configuration along with surrounding environmental conditions play a pivotal role in the electrocatalytic activity of Pt [9]. Two methods are extensively tried to increase the MOR activity and decrease the amount of Pt. The first theme is modification of the structure and/or morphology of Pt, like fabricating hollow or framed Pt structures [33] or using core-shell Pt configurations [34]. Secondly, exploiting Pt with metals like Co, Ni, and Sn. However, the Pt present in these catalysts is in the form of NPs with a diameter greater than 1 nm, leading to suboptimal mass activity. Further, Pt NPs are most likely to get poisoned by CO_{ads} in MOR [35], retarding their activity. Thus, the fabrication of new Pt-based MOR electrocatalysts with improved performance and poisoning resistance appears to be of significant practical and fundamental interest. Single-atom catalysts (SACs) recently

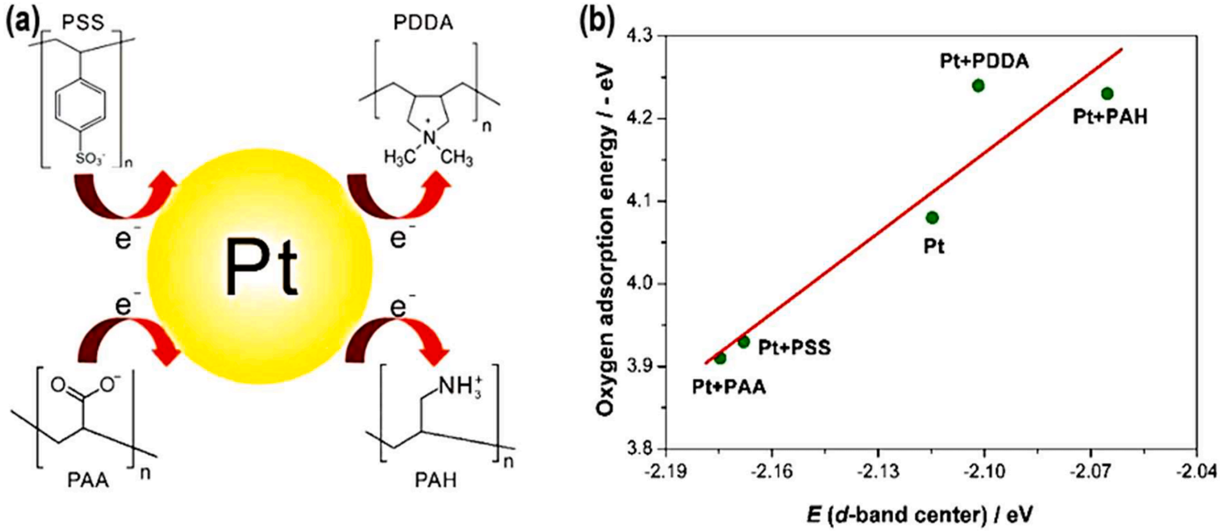

Fig. 3. (a) Possible modulation of Pt NP electron donor-acceptor behavior by polyanion (PSS) and polycation (PAA, PAH) functional groups, and (b) The d-band center of Pt slabs correlates with oxygen adsorption energy. Adapted with permission [29]. Copyright @2022, Elsevier.

surfaced as a new class of electrocatalysts with considerable potential in many electrocatalytic reactions like oxygen and hydrogen evolution, reduction of oxygen, CO_2, and N_2, as well as oxidation of hydrogen and formic acid. Pt SACs display remarkable efficiency in Pt utilization and have significant capability to catalyze CO oxidation [36]. Three adjacent Pt atoms are essential for the electrochemical dehydrogenation of methanol to CO in MOR. In addition, reports are there suggesting that SACs with single Pt atoms supporting CNTs are inactive towards MOR, where studies have been made on Pt active centres in isolation [37]. The catalytic performance of a single atom is considerably influenced by atomic coordination [38]. Earlier reports reveal that the manipulation of the bond between the single atom and substrate can modify the electronic structure and coordination of the central single atom [39,40]. For instance, Zhang et al. [41], immobilized the single Pt atoms on RuO_2 and carbon black (VXC-72) was achieved by a straightforward adsorption-impregnation preparation process (Fig. 4(a, b)). $Pt1/RuO_2$ SACs exhibited exceptional mass activity (6766 mA mg^{-1} Pt) and demonstrated remarkable stability towards MOR, surpassing the performance of the majority of previously established Pt-based catalysts (Fig. 4c). The mechanism of the MOR, which involves the dehydrogenation of methanol and electrooxidation of CO, has been investigated in greater detail using DFT calculations (Fig. 4(d–g)), validating the experimental findings that the synthesized SACs exhibit significant activity in the oxidation of alcohols. This discovery implies a potential strategy involving SACs for the application of direct alcohol fuel cells.

In another work, Li et al. [42] investigated the SANi-PtNWs (Fig. 5a) for MOR and EOR to comprehend more about their potential as multifunctional electrocatalysts. The synthesised SANi-PtNW displayed superior performance (3.87 A/mgPt) compared to the commercial Pt/C electrocatalyst (1.04 A/mgPt). In addition, the starting over potential of SANi-PtNWs (144 mV) is less than that of Pt/C, indicating a lower activation barrier for methanol oxidation on their surface. SANi-PtNW displays better performance than Pt/C for EOR in 1 M ethanol and 1 M KOH by a factor of 7 and 3, respectively. The long-term reliability of SANi-PtNW compared to pure Pt-NWs and Pt/C in MOR is shown in Fig. 5(b–g). DFT investigations revealed all reaction pathways as exothermic at experimental potential, and the concluding step of CO to CO_2 formation is facilitated by poor CO adsorption on SANi-modified Pt top-sites (by 0.06–0.28 eV) than Pt (111) top sites (Fig. 5f). Additional new information may be useful for single-atom tailoring to influence MOR or EOR activity.

3.2. Non-nobel metal-based catalysts

In order to catalyze MOR at practical level, it is desirable to develop novel catalysts that are not only cost-effective and easy to produce, but also highly efficient in catalytic activity, anti-CO ability, as well as durability. Therefore, the research is being perused on developing catalysts containing a lower proportion of noble metals for use in direct methanol fuel cell (DMFC) [43,44]. In this context, Co-oxides are the emerging catalysts of choice for HOR by virtue of their outstanding intrinsic features like structural and electrical flexibility, adjustable chemical characteristics, and redox rich chemistry. For instance, Jafarian et al. [45] prepared $Co(OH)_2$ modified glassy carbon (GC) electrode via anodic deposition and tested for methane oxidation reaction (MOR) activity. It was shown that cobalt existed in multiple valence states during the catalytic reaction, where Co (IV) state acted as the most active site for MOR. Further, Zafeiratos [46] investigated the structural effects of spinel Co_3O_4 and rock salt CoO on their HOR activity. The results indicated spinel Co_3O_4 to have more mobile O-lattice to initiate partial MOR by means of conversion of CH_3OH into HCHO. In another work, to improve the catalytic activity of Co_3O_4, Xia et al. [47], reported to have developed a 3D mesoporous Co_3O_4. This catalyst displayed much higher MOR activity as compared to non-porous Co_3O_4 because of large surface area (118–121 m^2/g).

On the other hand, Shahid et al. [48] published a rGO–Co_3O_4 composite for MOR in order to increase the conductivity of Co_3O_4 by utilizing nanocarbons such as reduced graphene oxide (rGO) (Fig. 6a(i)). When compared to bare Co_3O_4 material, rGO, and even the conventional Pt catalyst, the MOR activity of this catalyst was shown to be

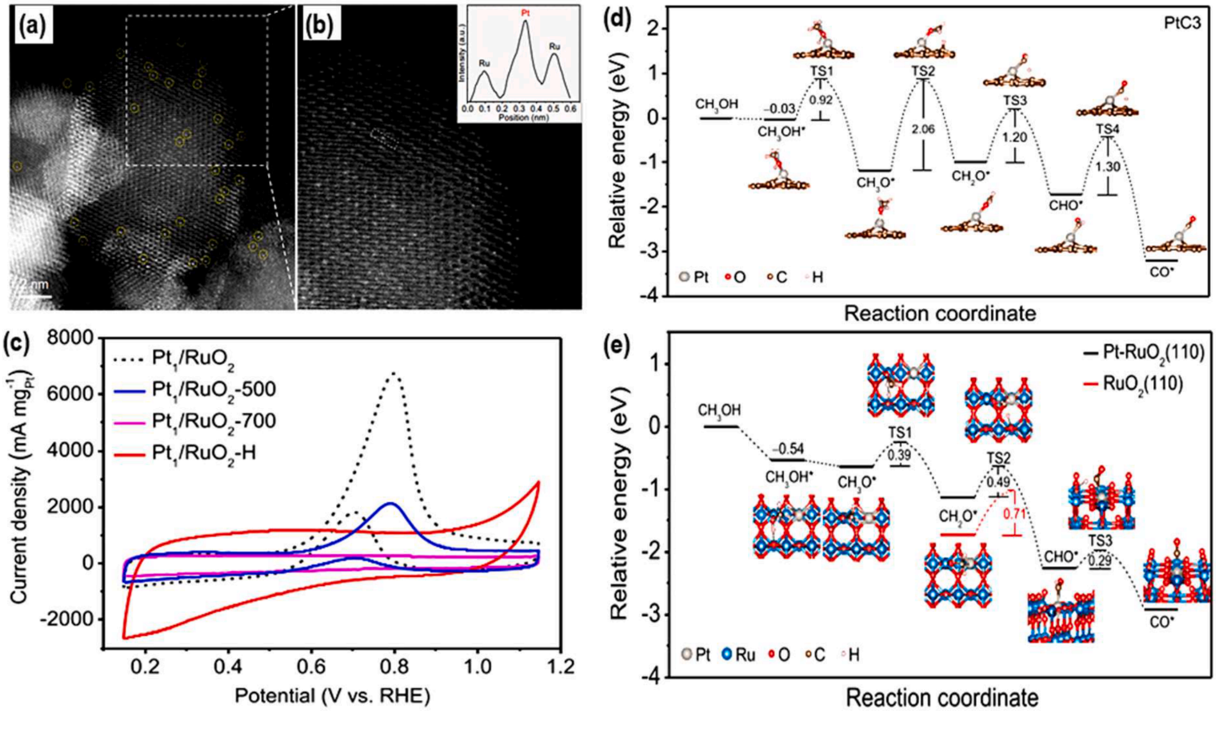

Fig. 4. (a, b) HAADF-STEM pictures for $Pt1/RuO_2$. (c) CV curves for various prepared $Pt1/RuO_2$ samples. (d) Calculated reaction free energy and energy barriers for MOR at PtC_3 catalysts. (e) Energy barriers for CO oxidation on Pt-RuO_2(110) and RuO_2(110). Adapted with permission [41]. Copyright @2021, Nature publishing group.

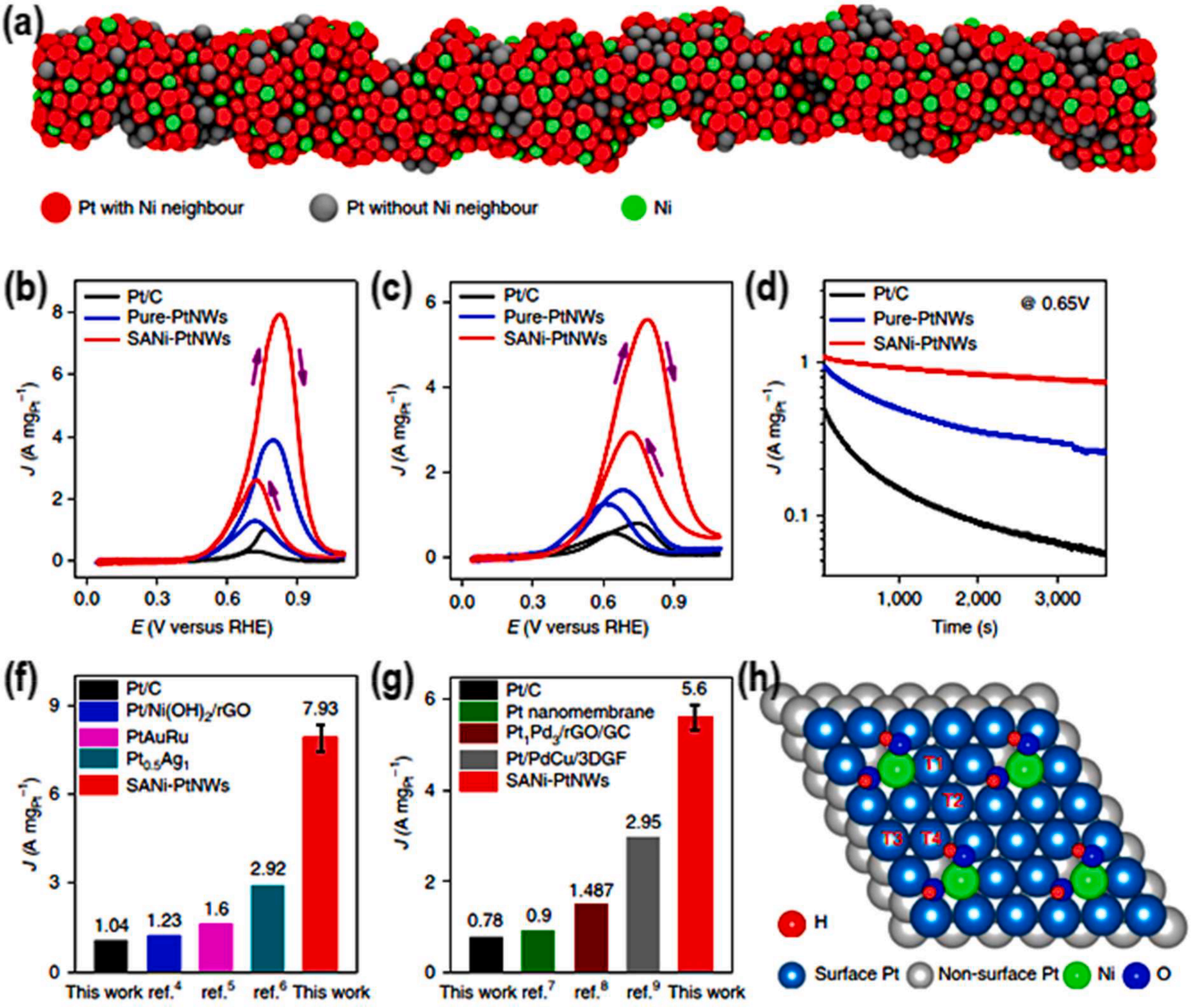

Fig. 5. (a) Schematic representation of SANi-PtNWs. CVs for (b) MOR, and (b) EOR, (d) Chronoamperometric MOR curves. (f, g) MOR and EOR current density comparison. (h) Theoretical model for SANi-decorated Pt (111) surface with different CO adsorption sites. Adapted with permission [42]. Copyright @2019, Nature publishing group.

significantly improved. It was determined that a content of 2% rGO would be optimal for the creation of an excellent version of catalyst, showing 362 mAcm^{-2} peak current density during MOR (Fig. 6a(ii)). Following the similar motive of enhanced conductivity of the catalyst, Thamer et al. [49] developed N-doped carbon nanofibers (Co/N—CNFs) via electrospinning strategy, and this material exhibited significant adsorption ability as well as low resistance towards electron transfer. While investigating the effect of N-content in the material using urea as N-source (0–5%), maximum activity for Co/N—CNFs was obtained with 4% N-content, displaying 100.84 mA/cm^2 higher than undoped-sample (63.56 mA/cm^2) (Fig. 6b(i-ii)).

4. Molecular catalysts for MOR

While numerous electrocatalysts, consisting of both noble-metal and non-noble-metal materials, have been employed for the MOR process, accurately determining the active site and overcoming obstacles in their chemical modification to achieve optimal performance remains a challenging task. On the other hand, molecular catalysts have well-defined active sites as well as distinct energy levels and easy chemical manipulation by substitution on the molecular core or replacing the central metal atom. Because of these characteristics, molecular systems might be seen as potential models for MOR [50]. For instance, Ru and Ni complexes are two catalysts widely used for selective oxidation of alcohol to aldehyde or acid [51]. In particular for MOR, various tetra-coordinated Ni complexes have been reported for MOR, as shown in Fig. 7.

For instance, Tanwar et al. [52]. combined bis-(iminopyridine) complexes with Ni/Co/Cr metal salts (Fig. 8a). Based on the results, it was shown that Co-based catalysts were more effective than Ni and Cr-based systems for electrocatalytic MOR process, with a high conversion rate of CH_3OH into sodium carbonate (up to 97% yield) and a 522.5 ± 13.5 mA cm^{-2} current density at 1.4 V (Fig. 8b). Fig. 8(c, d) further shows that the catalysts based on Co exhibited outstanding selectivity and durability. This research demonstrated that the molecular catalyst in a relatively homogeneous reaction mixture is primarily responsible for the electrocatalytic activity, with trace heterogeneous particles playing a minor role. This opens up new possibilities for the development of effective molecular-based MOR electrocatalysts.

Nevertheless, the molecular complexes have been found to breakdown in the electrolytic medium due to the hydrogenation of C = C and C = N moieties. This leads to the dissolution of metal active sites in the electrolyte, causing a loss in their electrocatalytic performance [4,16]. In order to tackle these problems, it was discovered that the integration of these molecular ligands into molecular organic frameworks is the most effective method to attain superior performance of molecular models in electrocatalytic MOR [54]. For instance, the MOR process could be efficiently improved using ZIF structures that contain a

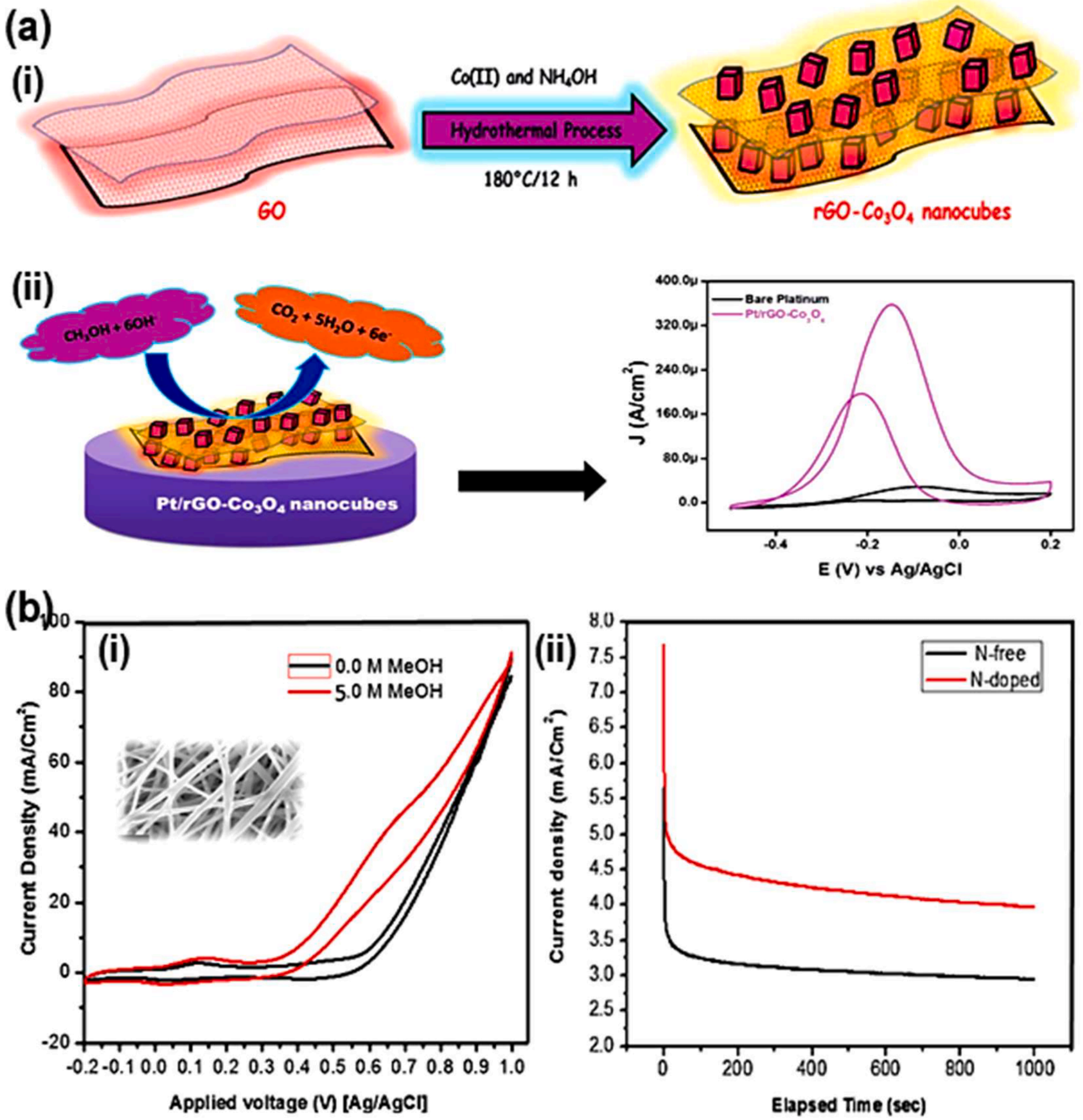

Fig. 6. (a) (i) Synthesis scheme for the rGO–Co_3O_4 nanocubes, (ii) MOR mechanism at Pt/rGO–Co_3O_4. Adapted with permission [48]. Copyright @2014, The Royal Society of Chemistry. (b) (i) Chronoamperometric investigation for Co/N—CNFs (4%) recorded in 1.0 M KOH after adding 3.0 M CH_3OH, (ii) CV curves of Co/N—CNFs recorded in 1 M KOH at 100 scan mV/s. Adapted with permission [49]. Copyright @2015, Elsevier.

tetrahedrally-coordinated redox-active central metal site linked with an imidazolate ligand. The carbon paste electrode doped with Ni-ZIF-8 had a current density of 0.744 $mAcm^{-2}$ in 0.1 M NaOH and 0.005 M MeOH at a potential of 1.71 V vs RHE [55]. The MOR was found to be caused by the presence of Ni (II) ions, which reacted with OH− to form $Ni(OH)_2$ via NiOOH, and the huge surface area of 1430 m^2g^{-1}. Despite the insufficient current density, the ZIF-8 based catalyst showed remarkable stability, retaining 98.6% of its original anodic current response even after 50 repeated cycles. In contrast to Zn-based ZIF-67, which is made up of a tetrahedrally coordinated Co site with an imidazolate ligand, it displayed a 2.5 $mAcm^{-2}$ current density at a potential of 1.71 V vs. RHE, which was somewhat greater in nano-porous Ni-doped ZIF-67 compared to Ni-doped ZIF-8 [56]. There were more active sites for MOR because of the bigger gaps for Ni loading in the highly porous Co-based MOF. In a similar vein, another approach involved impregnating porous Al-benzenetricarboxylate MIL-110 (MIL-110(Al)) with Ni [57]. The strong MOR activity was demonstrated by dissolving 20% Ni in MIL-110, which resulted in a current density of 14.4 $mAcm^{-2}$ at a potential of 1.71 V vs. RHE in 0.1 M NaOH and 0.1 M MeOH.

Hoseinie et al. [53] claimed to have created a ZIF-8-based electrocatalyst for MOR (Fig. 8e) using the same concept. In a mixed electrolyte of 0.5 M NaOH and 0.5 M MeOH, the produced ZIF-8-based catalyst showed a higher 32.7 $mAcm^{-2}$ current density in comparison to Pt-based catalysts (Fig. 8f). The findings showed that during the electrocatalytic MOR process, a large number of CH_3OH molecules could be easily diffused due to the constructed ZIF-8′s predicted cavity diameter of 1.22 nm (Fig. 8g). Additionally, the results showed that the ZIF-8 molecular system's backbone strain enhanced the proton acceptor nature, which greatly abstracted protons from methanol molecules and transported them to the ligand's N-atoms, resulting in effective MOR

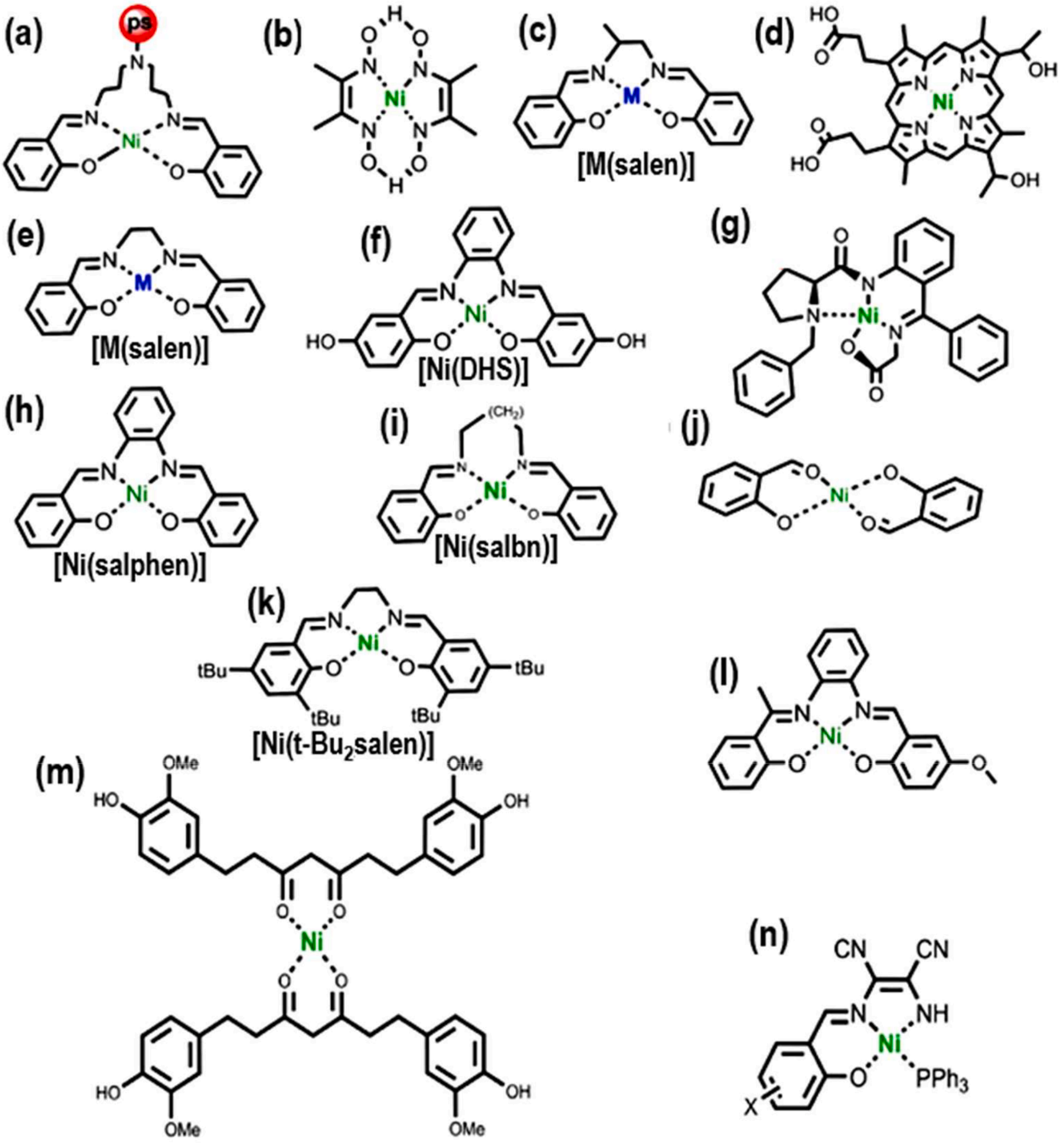

Fig. 7. Chemical structure of MOR significance coordination compounds.

activity [58].

The use of bimetallic MOFs, which exhibit faster charge transfer, has also shown encouraging MOR efficacy, in addition to monometallic MOFs. For instance, methanol electro-oxidation may benefit from the use of bimetallic MOFs containing Co and Ni. For instance, a NiCo-ZIF@-MoS_2 composite was reported by Liu and coworkers to be used as a GCE modifier and designed a CiNi-ZIF electrode material (Fig. 9) [59], displaying a redox couple at 0.42 V and 0.26 V in the absence of methanol, with the redox couples Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} being responsible for the oxidation and reduction, respectively. Moreover, the electrochemical response of the bimetallic MOF was demonstrated to be metal ion ratio dependent. With respect to current density, the bimetallic CoNi-ZIF (3:1) was superior to other ratios. In addition, a maximum current density of 72 mA was recorded at the electrode, and the electrode exhibited a linear response to varying methanol concentrations (0.2–0.7 M). The composite was tested as an active material for water splitting, and a current density of 10 mA was achieved at a potential of 1.55 V.

In another work, Rezaee et al. [60] reported that a NiCo-BDC MOF was employed as a sacrifice material to create a NiCo/NiO—CoO/nanoporous carbon composite that was then used to modify a GCE for methanol electro-oxidation (Fig. 10a). Direct pyrolysis of the bimetallic NiCo-MOF was used to synthesize the nanocomposite, as illustrated in Fig. 10a. The composite was examined in alkaline media with CV and demonstrated to have a maximum anodic current of 185 mA in the presence of MeOH (Fig. 10(b, c). The upgraded catalytic efficiency can be explained by the conductive features of the porous carbon framework and the generated metal oxides [61,62]. Direct synthesis of highly oxidative MOOH species from the metal oxides is proposed as the mechanism for the methanol electro-oxidation process (MOR) [60].

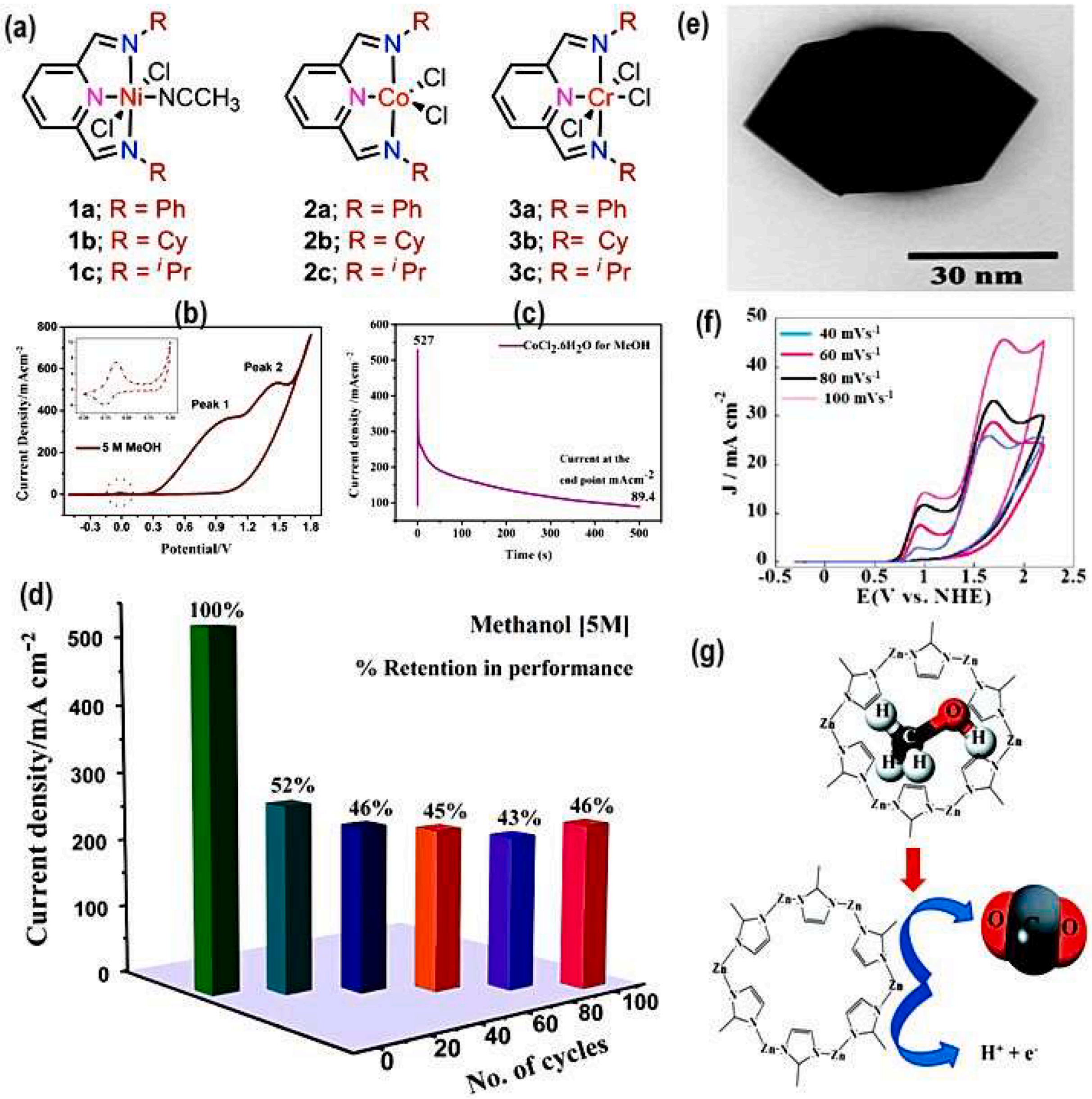

Fig. 8. The chemical structure of the NNN pincer-metal electrocatalysts, (b) CV plot, (c) The chronoamperometry plot, and (d) The cyclic stability recorded with 10 mM $CoCl_2 \cdot 6H_2O$ at 6 M NaOH and 5 M methanol. Taken from [52]. Copyright 2024, American Chemical Society. (e) TEM picture, (f) Scan rate dependent experimental curves, and (g) the proposed mechanism for the MOR, for prepared ZIF-8. Taken from [53]. Copyright 2019, The Royal Society of Chemistry.

Nevertheless, the catalysts based on MOF still exhibit inadequate electrical conductivity, which hampers the attainment of optimal performance. Within this framework, two methods have been utilized to enhance the catalytic efficiency of materials based on MOFs. These methods involve integrating MOFs with a conductive support, such as graphene, and subjecting MOFs to pyrolysis. For instance, a bi-metallic Ni-Cu benzenedicarboxylate MOF was incorporated with reduced graphene oxide to improve the catalytic MOR performance of a bare bi-metallic MOF [63]. In a similar way, two Ni-based MOFs, CTGU-17 and CTGU-18, which were pseudo-isomeric and linked with 1,4-naphthalenedicarboxylate and 4,4′-dipyridyl amine, respectively, were fabricated to improve the catalytic MOR performance [64], (Fig. 11(a, b)). The CTGU-18/AB (AB stands for acetylene black) mixture showed the best MOR results, displaying maximal MOR performance of 442.3 $mAmg^{-1}$ in 0.1 mol L^{-1} KOH and 1 mol L^{-1} MeOH at 1.66 V vs RHE (Fig. 11c). The increased MOR activity was described as a result of a synergistic interaction between CTGU-18 and active $[Ni_2(COO)_4N_2]$ motifs. A full inventory of MOF-based catalysts and their respective performances is presented in Table 1.

On the other hand, the pyrolyzed MOFs-based material possesses a 3D network structure that exhibits both a large surface area and a high degree of graphitization. This makes it a promising catalyst for the electrocatalytic MOR process in the future [54,78]. The MOFs underwent pyrolysis and N-doping (via imidazole linkers) allowed the resulted catalysts for interaction with CH3OH through hydrogen bonds, and thereby resulting in an improvement in charge mobility for the MOR process. For instance, Pd was loaded with Cu on carbon support (Pd-Cu/C) by calcinating a Cu-benzenedicarboxylate MOF (HKUST-1) in an inert environment [72]. Fig. 11d depicts the schematic of the synthesis technique for Pd-Cu/C catalyst. The prepared catalyst exhibited remarkable MOR activity with 4643 $mAmg^{-1}$ current density at a potential of 1.10 V vs RHE in a solution containing 1 M KOH and 1 M MeOH (Fig. 11e). The catalytic activity of Pd-Cu/C in the MOR process was found to be 13 times higher than that of commercial Pd/C, because

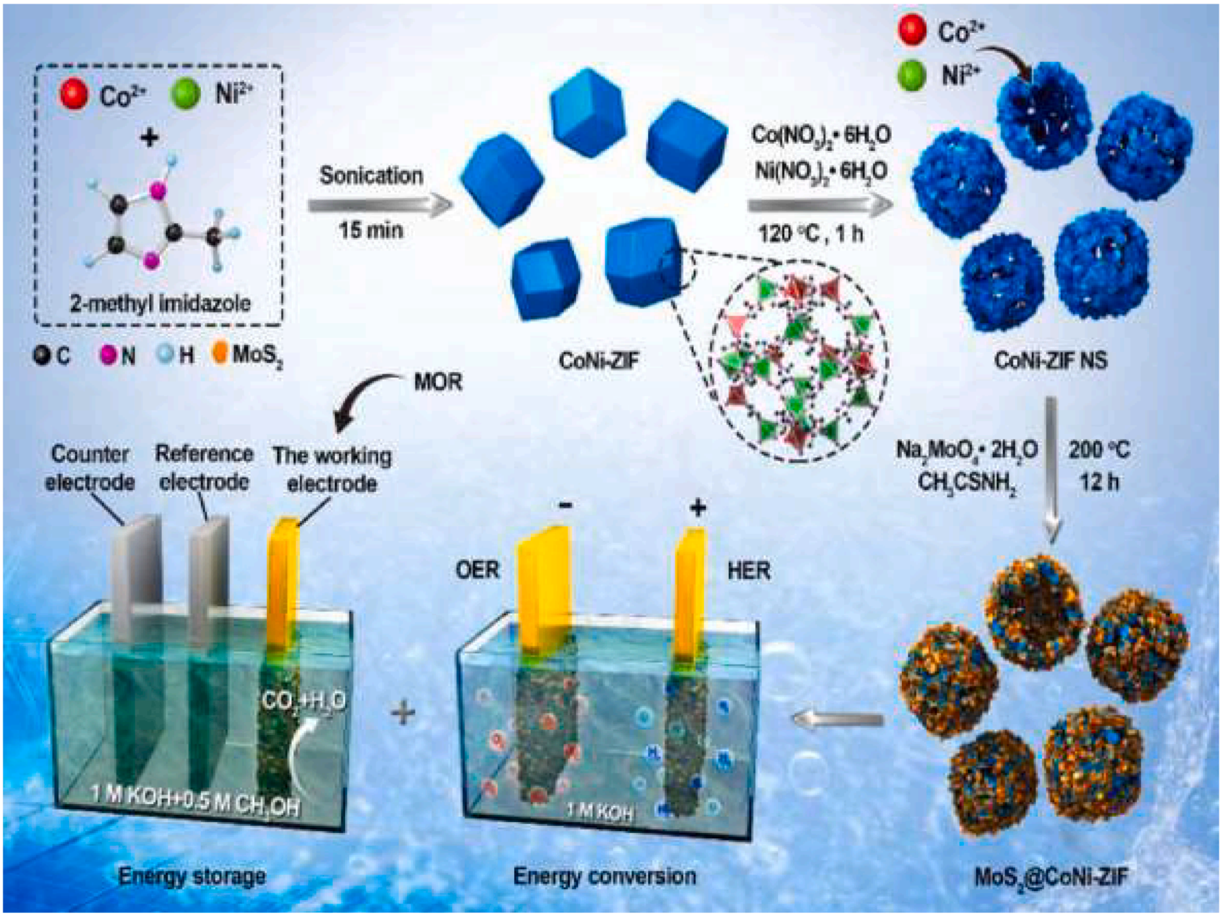

Fig. 9. Preparation approach for CoNi-ZIF and its application in MOR, HER, and OER. Adapted with permission [59]. Copyright @2019, Elsevier.

Cu has a stronger binding affinity for CO than Pd, which protects the electrode against CO poisoning (Fig. 11f).

5. Conclusions

In conclusion, this review focused on the methanol oxidation processes utilizing molecular catalysts along with noble and non-noble metal-based materials. For both noble and non-noble transition metal-based electrocatalysts, attaching the metal nanoparticles to carbon or hetero-atom-doped carbon supports enhances their dispersion and electrical conductivity to the active sites. This facilitates the adsorption of methanol oxidation reaction intermediates, resulting in improved catalytic activity and stability for these catalysts. Moreover, the progress of Pt-based catalysts relies on unraveling the mechanism and kinetics of methanol oxidation process on individual metal atoms and/or nanoparticles. Metal electrocatalysts supported on a carbon substrate can vary in size from individual atoms to nanoparticles or clusters, subject to a certain set of limitations. Furthermore, it is necessary to enhance the loading and endurance of single-atom catalysts in order to optimize their installation in fuel cells. Instead of placing them on the surface, a small number of individual atoms are incorporated into the carbon material. This atomic loading can enhance gas phase deposition or create a unique structure with a weight percentage of up to 17% carbon. This reduces the electrical effects on supporting single-atom catalysts. Nevertheless, these catalysts still need to overcome the challenges of CO poisoning of active sites, restricted activity, and selectivity. In order for MOR to proceed, the indirect oxidation pathway necessitates a Pt ensemble consisting of neighboring atoms. Therefore, the utilization of dual- and multi-site electrocatalysts enhances the efficiency of methanol oxidation processes. However, the synthesis of catalysts with precise dual or multi-active sites is a formidable challenge.

In contrast, molecular catalysts are easier to chemically manipulate by substituting the molecular core or replacing the central metal atom; they also have clearly defined active sites and unique energy levels. Due to these features, these catalysts could be considered as possible catalytic models for the methanol oxidation process. The significant enhancement in catalytic activity and endurance of the molecular catalysts can be attributed to the synergistic effect between the single-metal site and the molecular framework. Moreover, these electrocatalysts can also stop CO production during catalytic methanol oxidation. This speeds up the process of changing methanol into CO_2 by making the catalytic active sites active again. However, the electrolytic medium causes the molecular complexes to break down through the hydrogenation of their functional groups. Because of this, the electrolyte dissolves the metal active sites, rendering them ineffective as electrocatalysts. The best way to improve the electrocatalytic methanol oxidation performance of molecular models is to incorporate the molecular organic framework. However, molecular organic framework-based catalysts still have poor electrical conductivity as well as methanol tolerance which makes it hard to get their best performance. Integrating these catalysts with nanocarbon supports and treating them at high temperatures is a good way to make them work better as catalysts.

Overall, despite the fact that many heterogenous as well as molecular catalysts have been employed for the methanol oxidation reaction, there are still many challenges to be solve to approach the practical application of direct methanol fuel cells. Herein, we discussed the major challenges and future prospects for the development of efficient and inexpensive catalysts as well as direct methanol fuel cells. Firstly, it is necessary to comprehend the catalytic methanol oxidation reaction

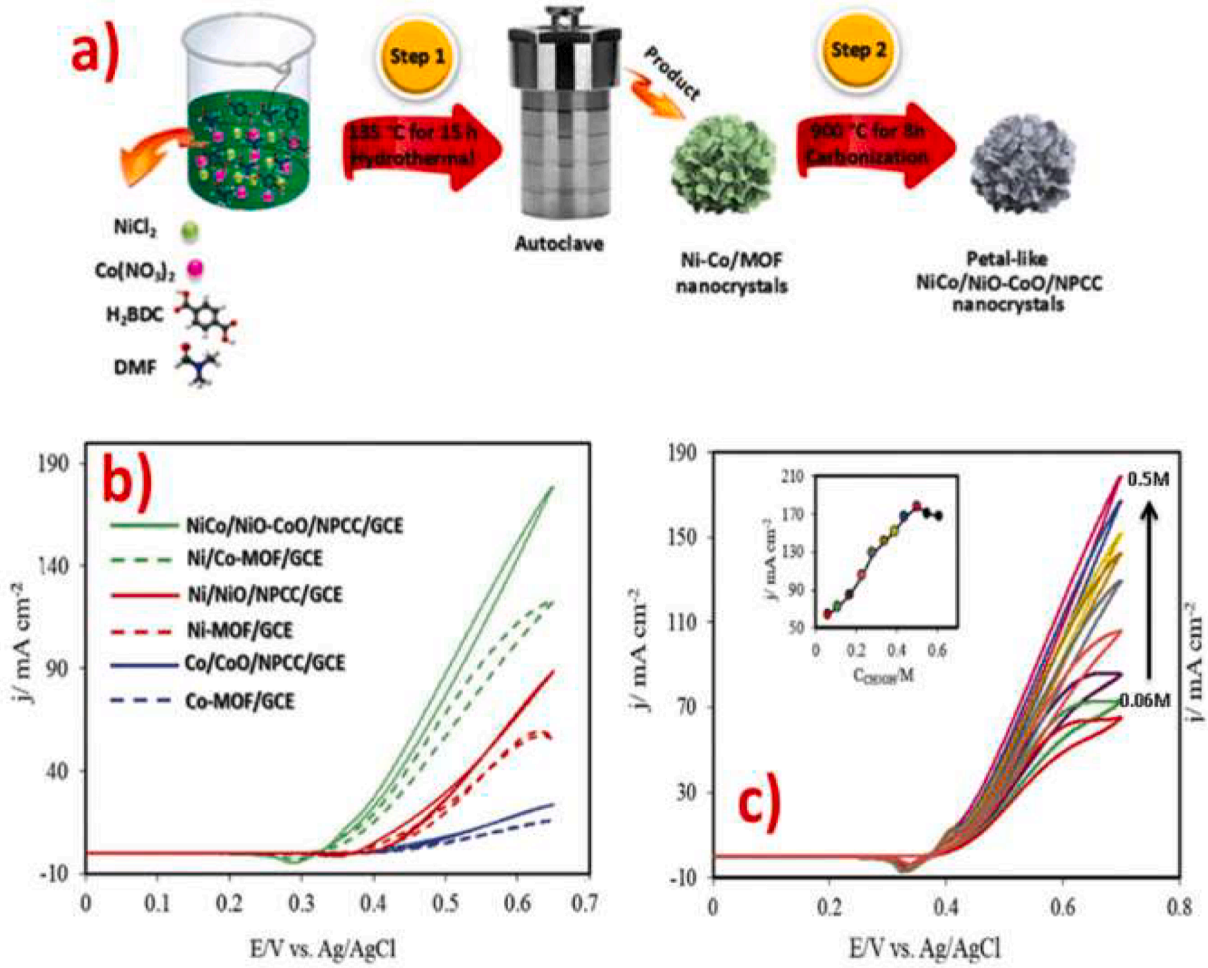

Fig. 10. (a) Preparation strategy, CVs (b) in absence of MeOH, (c) in presence of MeOH, for NiCo/NiO—CoO/NPCC composites. Adapted with permission [60]. Copyright @2019, Elsevier.

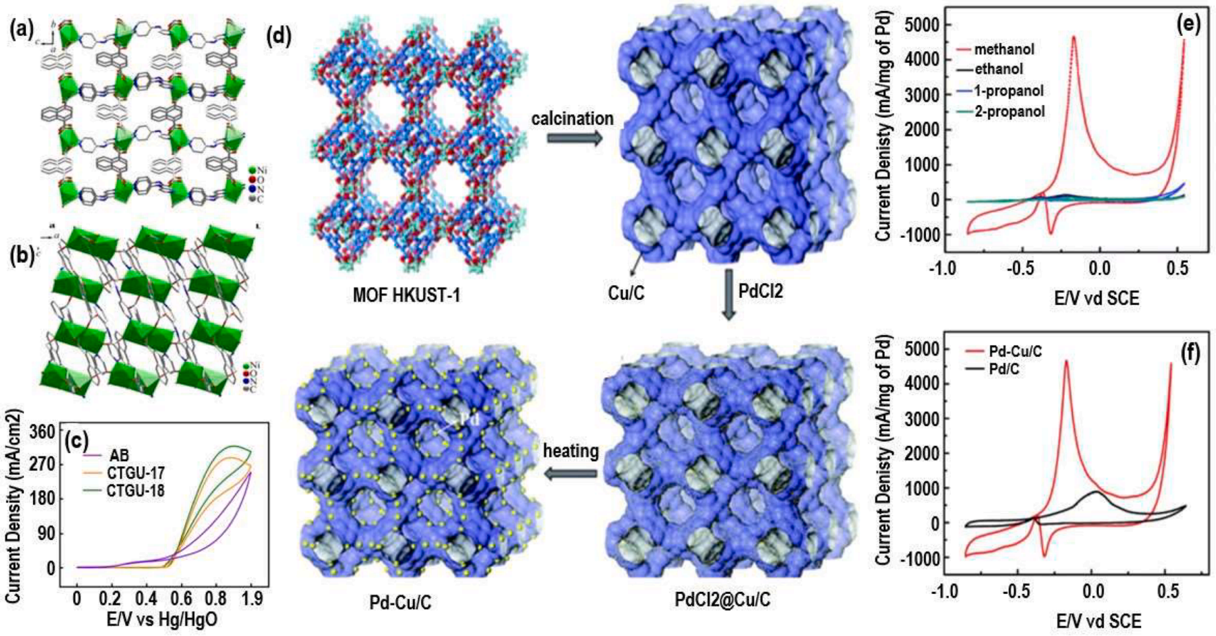

Fig. 11. (a, b) The crystal structure of the prepared CTGU-17 and CTGU-18, and (c) their MOR activities recorded in 0.1 molL^{-1} KOH and 1.0 molL^{-1} CH_3OH @ 50 mVs^{-1} scan rate. Taken from [64]. Copyright 2020, Springer. (d) A systematic illustration of the preparation protocol for the Pd-Cu/C catalyst using HKUST-1, (e, f) The alcohol activity of the prepared catalyst. Taken from [72]. Copyright 2018, The Royal Society of Chemistry.

Table 1
MOR activity data of various MOFs-Derived electrocatalysts.

Catalyst	Measurement Conditions	MOR Activity Current Density	Potential V vs RHE	Refs.
Pt/NPC800	0.5 M H_2SO_4/0.5 M CH_3OH	5 mA/cm^2	0.88 V	[65]
PtCo/NCS	0.5 M H_2SO_4/0.5 M CH_3OH	1.25 mA/cm^2	0.34 V	[66]
Pt/Co@NCNTs-MC800	0.5 M H_2SO_4/0.5 M CH_3OH	700.3 mA/mg	2.59 V	[67]
Cu@Pt/C	0.5 M H_2SO_4/0.5 M CH_3OH	624 mA/cm^2/ mg Pt	2.59 V	[68]
PtNi/C	0.5 M H_2SO_4/0.5 M CH_3OH	27.28 mA/cm^2	0.88 V	[69]
Pt/Ru/NMPCs	0.5 M H_2SO_4/0.5 M CH_3OH	435.8 mA/mg	0.21 V	[70]
Pd/ZC-1000	0.5 M H_2SO_4/0.5 M CH_3OH	45.20 mA/mg	1.25 V	[71]
Pd-Cu/C	0.5 M H_2SO_4/0.5 M CH_3OH	4643 mA/mg Pd	1.10 V	[72]
Pt_3Fe Over Carbon	0.5 M H_2SO_4/0.5 M CH_3OH	50 mA/mg	0.75 V	[73]
MOF Derived Oxides CoCu	1 M KOH/1 M CH_3OH	419 Ag	1.66 V	[74]
$Ni_xCo_{3-x}O_{4-y}$	1 M KOH/1 M CH_3OH	200 Ag	1.41 V	[75]
NF/Co_30_4/ $NiCo_20_4$	1 M KOH/0.5 M CH_3OH	140 mA/cm^2	1.46 V	[76]
NiCo/NiO—CoO	0.5 M NaOH/0.5 M CH_3OH	178 mA/mg Pt	0.84 V	[60]
Pt-WC/$W_{24}O_{60}$/ NC_{z8}	0.5 M H_2SO_4/0.5 M CH_3OH	2492.2 mA/ mgPt	2.59 V	[77]
Pt/$W_{18}O_{49}$	0.5 M H_2SO_4/0.5 M CH_3OH	1.15 mA/cm^2 Pt	2.59 V	[140]
ZnO@Ta_2O_5	1 M KOH/0.5 M CH_3OH	117 mA/cm^2	1.56 V	[141]

mechanism at the atomic level. Developing a series of suitable molecular catalysts and learning lessons should be applied to develop efficient heterogeneous catalysts with well-defined structural-activity correlations as well as catalytic mechanisms with the help of advanced characterization techniques and theoretical optimizations. Moreover, the rate and mechanism of electrochemical reactions in fuel cells are directly influenced by the adsorption process and the subsequent interaction of reactants and products with electrocatalysts. These facts are closely tied to the acidity or alkalinity of the fuel cell electrolyte membrane, which can function as either a proton (H^+) conductor or a hydroxide (OH^-) conductor. The rate of reaction is influenced by the pH because of the interaction between OH_{ads} species and OH-ions, which affects the structure of the reactant and the bonding energy between the organic adsorbate and the catalyst surface. Although it is stable and strong, an anion exchange electrolyte membrane with high anion conductivity is very hard to work with when making alkaline methanol fuel cells. The crystallization of alkaline metal carbonate and bicarbonate in the electrolyte-filled pores is another drawback that hinders ionic transport. The poor stability of the membrane poses challenges for alkaline electrolyte-based fuel cells to operate at high temperatures. Furthermore, the utilization of a cathode methanol-tolerant electrocatalyst in a direct methanol fuel cell facilitates the reduction of methanol crossover resistance. Utilizing an active material that is capable of withstanding the presence of methanol is a straightforward approach to modifying the effectiveness and specificity of heterogeneous catalysts for the oxidation of methanol in direct methanol fuel cells. The electrical features of the catalyst's surface can be adjusted by incorporating the P-S/C support with the noble or non-noble metallic active sites. The development of the P-S/C-based heterogeneous transition metal catalyst not only simplifies the design of DMFC devices and reduces the need for costly proton membranes, but also enables the achievement of high catalytic selectivity and effective resistance against the detrimental effects of methanol permeability.

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CRediT authorship contribution statement

Monika Singh: Writing – original draft, Investigation, Formal analysis, Conceptualization. **Hari Mohan Sharma:** Writing – review & editing, Formal analysis. **Jasvinder Kaur:** Writing – review & editing. **Dipak Kumar Das:** Writing – review & editing, Validation, Supervision. **Mohd Ubaidullah:** Writing – review & editing. **Ram K. Gupta:** Writing – review & editing, Visualization, Validation, Project administration, Supervision. **Anuj Kumar:** Writing – review & editing, Project administration, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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