Molybdenum carbide nanoparticle: Understanding the surface properties and reaction mechanism for energy production towards a sustainable future

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Abstract

Rational design and synthesis of cheap, noble metal-free, thermal/hydrothermal stable and active catalyst for efficient hydrogenation and hydrogen production reaction is crucial towards renewable and sustainable energy generation. This gives the use of molybdenum carbide nanoparticle considerable attention as an alternative to noble metals. However, the industrial application is not yet feasible due to insufficient stability and activity coupled with the lack of detailed understanding of the reaction mechanism. This work discusses the effect of the operating parameters on the properties and morphology of molybdenum carbide nanoparticle, as well as their impact on the catalytic activity. Critical issues such as structural diversity, surface properties, and multiscale reaction modeling are also discussed for better understanding of the reaction mechanism. This is a promising strategy towards synthesis of cost-effective and efficient catalysts for renewable and sustainable energy production.

1. Introduction

One of the most important research gaps in the field of renewable and sustainable energy is rational design and synthesis of suitable eco-friendly and cost-effective catalysts with preserved energy and chemical functionality for prolonged applications in several industrial processes [1–3]. The unique chemical and physical properties of molybdenum carbide nanoparticle [4] have enhanced its popularity in the fields of materials and chemical science towards production of renewable and sustainable energy [5]. The outstanding properties of MCN include thermal stability, high electrical conductivity, adsorption capacity, high melting point, and hardness [6]. Moreover, the characteristics of MCNs such as resistance to nitrogen and sulfur, high catalytic current density, and durability are similar to those of noble metals, which enable their utilization in hydrogenation and hydrogen evolution reactions (HER) [7,8]. Examples of these reactions include CO₂ hydrogenation to alcohol, CO hydrogenation to alcohol [9], hydrodeoxygenation [10], electrocatalytic hydrogen evolution from water splitting [11] including oxygen evolution reaction [12], hydro-treating [13], watergas shift reaction (WGS) [14], hydro-desulfurization (HDS) [15], CH₄ aromatization [16], and hydrodenitrogenation (HDN) [17]. The MCNs are also suitable for electrocatalytic reactions.

MCN has been used successfully to hydrogenate feedstock such as cellulose, indole, toluene, and cumene, which are popularly processed with group 9 and 10 noble metals (Pt, Pd, Rh) [18–20]. These being commercially available catalysts for reactions such as methane reforming, hydrocarbon isomerization, water-gas shift reactions, and CO hydrogenation. Further, MCN has been employed as an alternative to Ru, and to an extent Pt as electrocatalysts in the anode of polymer membrane fuel cells (PEMFC) [21–23] because of its platinum-like behaviors [24]. The thermal stability of MCN in the absence of oxygen is due to the delay of the sintering and attrition effects as reaction proceeds. However, the catalytic activity of MCN systems mainly depends on the nature and physiochemical properties of the catalyst.

Previously, the high temperature classical metallurgical process was used to prepare metal carbides but the products exhibit low specific surface areas and high particle size [25]. This results in the Metal carbide products exhibiting low catalytic performance in targeted catalytic processes [3]. Currently, the MCN synthesis method by Lee et al. [26], which is a temperature program reduction (TPR) carburization is most popular due to its remarkable improvement on the textural property of the product [27]. TPR carburization is a carbothermal reduction method that carburizes the Mo precursor supported on carbon in hydrogen atmosphere [28]. The Mo precursor is to be thermally treated, at increasing the controlled temperature in a reducing environment [29]. To form the carbide phase, the carbon source is mainly
light hydrocarbon, while hydrogen is the reducing agent. The essence of the controlled temperature is to optimize the carburation temperature to avoid sintering of the reduced Mo particles, thereby reducing the particle size of the resulting carbide. The carburization conditions (temperature and time) control the physiochemical properties, the chemical nature, and structure of the resulting carbide phase. MCN exists in two main crystalline structures: orthorhombic and hexagonal (Mo₂C) and hexagonal structure. The preparation methods of carbide-supported metal catalysts include wet impregnation [30], atomic layer deposition [31] and vacuum environment [32]. Mostly, the synthesized MCN, passivated prior to its exposure to air to prevent oxidation.

The goal of this review is to provide insight into the surface properties of MCN and its reaction mechanism for renewable and sustainable energy production towards a sustainable future. In Section 2, rational design and synthesis of MCN are discussed, highlighting the effect of operating parameters. The third section deals with a structural diversity of MCN using density functional theory (DFT) to categorize different forms of MCN based on structural differences. Section 4 briefly discusses the surface properties of MCNs to determine the stability based on their structural diversity. While Section 5 gives an insight into multiscale reaction model on MCNs for a better understanding of catalytic reaction mechanism of the system, which is crucial to the commercial applications of MCN in the production of renewable and sustainable energy. Finally, we presented the catalytic activity of MCN based catalysts (both unsupported and promoted/supported) in Section 6.

2. Preparation of MCN

MCNs are popularly prepared by carbothermal reduction carburization process. This process consists of three different steps; (i) deposition of the Mo-precursor on the carbon source, (ii) carbothermal reduction of the Mo-precursor to produce MCN, and [33] the subsequent stabilization of the produced MCN by Mo-carbide surface passivation [19]. Generally, synthesis of MoO₂ nanoparticles is not a difficult task; the transformation into MCN is where the major challenge is. The transformation is so complex due to the influence of several variables. Experimentally, different kind of MCN is prepared using various strategies. These strategies include direct carburization of MoO₃ by 10–20% CH₄–H₂ mixtures at 750 °C for 4 h to produce thermodynamically stable hexagonal Mo₂C [34]; reduction of MoO₃ by NH₃ to produce MoN and then carburization of MoN by using CH₄–H₂ mixture to produce orthorhombic MoC [35] reduction and carburization of belt-shaped α-MoO₃ by using 5% n-C₄H₁₀–H₂ mixture at 700 °C for 4 h to produce metastable phase face-centered cubic (fcc) α-MoC₁₋ₓ [36]; solid-state reaction in combination with H₂ reduction at 800° C to form hexagonal Mo₂C at 20 min reduction time and hexagonal α-MoC at 10 min reduction time using glucose as the carbon source [37]. However, carburization with a 10% C₃H₆–H₂ mixture produces in mixed crystal phases [36]. All the phases can be differentiated and identified with ease. MCN can also be synthesized via reactive hard templating, a technique where a precursor such as MoCl₅ is used with mpg-C₃N₄ as a template in ratio 1:1 in ethanol solution (Eq. (1)) [38].

\[
(MoCl₅ + 2C₂H₅OH → MoCl₅(OH)₂C₃H₆ + 2HCl) \tag{1}
\]

Furthermore, Hare et al. [39] and Saito et al., [40] used arc discharge method to prepared β-Mo₂C and α-Mo₂C encapsulated with polyaromatic carbon. The most efficient and common strategy for MCN production is high temperatures reduction and carburization of MoO₃ by a mixture of hydrocarbon and hydrogen. The major advantages of this strategy are the formation of a pure crystal phase and avoidance of contamination by coke. Typically, the crystalline phase can be controlled by reconciling the gas composition of the reducing and carburizing agent [41]. However, the effect of the operating parameters has not been significantly explored. The synthesized MCN normally possess random size distribution, which ranges from few nanometers to several hundred nanometers with irregular shapes [42].

2.1. Effect of operating parameters on the nature of MCN

The effect of carburization conditions such as carbon source, pre-treatment temperature Tpre℃, heating rate, Mo loading, carburization time (tcarb), carburization temperature (Tcarb), Mo-precursor and crystalline phases is vital on the MCN crystalline Mo-phases. The effect could be analyzed by comparing the measured H₂-consumption from TPR results and the crystallinity of the carburized samples via XRD analysis.

2.1.1. Carbon source

The morphology of MCN is highly sensitive to the choice of hydrocarbon used. Mo et al. [43] reported that a high concentration of carbon source such as long chain hydrocarbon favors the formation of MoC (with face-centered cubic (fcc)) and nanosized Mo₂C (with hexagonal closest-packed (hcp)) due to the severity of carbon deposition at high carburization temperature. The deposited carbon may block the mesopores to form new micropores [43]. Further, increasing the chain length of the carbon source lessens the particle size and the required carburization temperature for MCN synthesis [41]. The use of low concentration of small chain hydrocarbon leads to agglomeration of carbide particles at a low heating rate. Prominent among the carbon sources are 20% CH₄–H₂ to form hexagonal close-packed MCN, 5% n-C₃H₁₀–H₂ to form fcc MCN, 10% C₄H₁₀–H₂ to form mixed crystal phases by the reducing and carburizing the precursor. The MCN synthesized with C₂H₆–H₂ as the carburizing agent exhibits the roughest surface and highest adsorption capacity for H₂, while synthesized with n-C₃H₁₀–H₂ exhibits a very condensed surface [41]. Recently, Tang et al. [37]
explored the use of glucose as a cheap and environmentally benign carbon source. They successfully produced MCN with a high surface area by using a facile solid-state reaction together with H₂ reduction at 800 °C.

2.1.2. Pre-treatment temperature

The influence of pre-treatment temperature plays a vital role in carburation and crystallinity of MCN. Ma et al. [44] revealed that pre-treating the precursors helps to achieve a complete carburation at a lower temperature compared to untreated samples. Guille-Lopez et al. [19] studied the effect of pre-treatment temperature on MCN obtained at 10% Mo loading, 710 °C TPreT and tPreT of 60 min in an argon stream. Two different TPreT 250 and 550 °C were used to produce samples E-11 and E-12 respectively. The TPR-H₂ consumption profile showed that sample E-11 exhibited two different sharp peaks. A low-temperature peak and an incomplete high-temperature peak (Fig. 1a), which indicates incomplete carburation. Meanwhile, sample E-12 has no sharp peak at low temperature because Mo⁶⁺ completely reduced to Mo⁴⁺ as the pretreatment proceeds at 550 °C. Moreover, the unfinished carburation of sample E-11 is mainly because its carburation commenced at a temperature (635 °C) higher than that of E-12 (600 °C).

Further, the unfinished carburation of E-11 lead to the formation of a large amount of crystalline MoO₂ phase rather than MCN as presented in the samples XRD pattern (Fig. 1b). A few traces of MCN and graphite, which corresponds to the carbon source were also present. However, the XRD pattern of sample E-12 shows that the sample is predominantly MCN with a trace of graphite due to complete carburation of the precursor. Therefore, low-temperature pretreatment speeds up the carburation reaction of Mo⁰ rather than a reduction of MoO₂.

2.1.3. Heating rate

Guille-Lopez et al. [15] investigated the effect of heating rate on the formation of MCN at 20% Mo loading, TPreT = 840 °C, and tPreT = 5 min in an argon stream. Two different types of carburation experiments were used to produce sample E-2 and E-10 respectively. The first carburation was done at 10 °C/min till the TCarb from room temperature while maintaining tCarb. The second type was conducted at 10 °C/min till 550 °C and successively heated at 3 °C/min from 550 °C to TCarb. The TPR-H₂ consumption profile shows that both samples have two different complete sharp peaks. A low-temperature peak and a high-temperature peak (Fig. 2a). Moreover, the carburation of sample E-10 commences at a temperature (575 °C) earlier compared to that of E-2 (618 °C) and the peak temperatures are 693 and 760 °C (Fig. 2a). This shows that the carburation of the sample is favored by low heating rate [29] as in E-10. From the XRD pattern (Fig. 2b), it is evident that both samples are majorly MCN with a trace of graphite from the carbon source. However, E-10 exhibits higher MCN particle size than E-2 due to sintering of the carbide phase of the sample, induced by high temperature.

2.1.4. Carburation temperature

One of the major requirement for synthesis of MCN, which makes it difficult to reproduce and control the desired particle size and surface area is high temperatures [34]. Guille-Lopez et al. [15] did an extensive study on the effect carburation temperature on the crystalline phases of MCN at 50% Mo loading, 250 °C TPreT and tPreT of 5 min using heating of 10 °C/min in an argon stream. The samples were carburated at four different TCarb = 500, 650, 700 and 840 °C to form sample E-6, E-7, E-8 and E-1 respectively (Fig. 3). All the samples exhibit only one peak at low temperature except E-1 that has another incomplete peak at high temperature. Further, the low-temperature peak of E-6 is incomplete, while it terminated at about T = 600 °C for E-7, and E-8. This indicates that samples E-6, E-7, and E-8 are mainly Mo₂C with a trace of Mo₆⁺ for sample E-8, while E-1 comprises of MCN, Mo⁰ and MoO₂. The presence of MoO₂ and Mo₆⁺ in E-1 is due to incomplete carburation at the high-temperature peak. The XRD patterns of the samples also confirm the composition of the samples (Fig. 3b). The incomplete carburation of E-1 is because of insufficient carburation time. However, several researchers like Guzmán et al. [34], Xiao et al. [41], Mo et al. [43] were able to achieve complete carburation at low temperature but at a reasonable length of time. Therefore, it is tenable to deduce that low-temperature carburation is visible at a reasonable length of carburation time. This claim is well proven in the next subsection.

2.1.5. Carburation time (tCarb)

Fine-tuning tCarb, with other parameters like TCarb is crucial towards achieving a completely carburized MCN phase [34]. The study of Guille-Lopez et al. [15] investigates the effect of tCarb on the carburation and crystallinity of MCN. The samples pre-treated at 200 °C containing 50 wt% Mo was carburated using heating rate of 10 °C/min to 840 °C at a different time of 5 and 60 min for samples E-1 and E-9 respectively (Fig. 4). Fig. 4a shows that 5 min carburation (E-1) exhibits an incomplete carburation, while the carburation was completed for E-9. Therefore, a long tCarb is essential for a complete carburation at 840 °C due to low carburation rate. The composition of the two samples is vivid in Fig. 4b. Sample E-1 comprises of crystalline phases of MCN, MoO₂ and Mo⁰ while E-9 is purely MCN crystalline phase. The presence of MoO₂ and Mo⁰ in E-1 is due to the incomplete carburation.

2.1.6. Carbon/metal ratio

Carbon/metal ratio plays a vital role in the design of MCN due to its remarkable impact on the chemical and catalytic properties. The increase in carbon/metal ratio leads to a decrease in adsorption energy but an increase in the dissociation barrier. The study of Posada-Perez et al. [45], shows that an increase in the carbon content of MCN from Mo₂C to Mo₆+C results in the reactivity of the Mo centers because the MoC surface is saturated and less metallic, while that of Mo₆+C is unsaturated and more metallic [46]. Although, the Mo centers are still capable of binding CO₂ molecule effectively without breakage of the second C–O bond, the cleavage of the first C–O bond need to be supported by hydrogen as shown below [47]:

\[
\text{H} + \text{OCO} \rightarrow \text{HOCO} \rightarrow \text{HO} + \text{CO}
\]

Consequently, Mo₆+C is a selective catalyst for reduction of CO₂ to CH₃OH. The remarkable impact of carbon/metal ratio on catalytic and chemical properties of MCN is illustrated in Fig. 5.

The rate of production of CH₃OH increases as the ratio increases from Mo₂C to Mo₆+C making Mo₆+C a better catalyst for the system.
Therefore, MoC is a viable and selective catalyst for high temperatures synthesis of CH₃OH.

2.2. Surface carbon species

The surface carbon species [48] of MCN comprises of free carbon, adsorptive carbon, and carbide carbon. The free carbon could be pyrolytic or graphitic carbon, left on the MCN surface during high-temperature hydrocarbon degradation. Graphitic carbon exhibits a higher graphitization degree than the pyrolytic carbon [49,50]. The adsorptive carbon is the weakly adsorbed matter for instance bonded molecules of CO and CO₂ [51]. The carbide carbon is the native carbon, which could be carbon-terminated Mo₂C and the strong adsorptive CS like the one attributed to disassociation of adsorbed feedstock. The report of Mo et al. [43] indicates that the graphitic carbide, adsorptive, and pyrolytic were in the range of 200–300, 460–490, 600–690 and 700–800 °C, respectively on MCN surface based on temperature-programmed hydrogenation (TPH) (Fig. 6).

3. Structural diversity of molybdenum carbide

Understanding the structural diversity of MCN is an uphill task due to its complex nature and a number of metastable and stable phases [52]. However, density functional theory (DFT) based estimations with the revised Perdew–Burke–Ernzerhof (RPBE) exchange-correlation functional has been successfully employed to identify the crystal structure [53]. MCN is characterized by five different crystal structures: α-Mo₂C, β-Mo₂C, γ-MoC and η-MoC [54], which arise from different preparation methods as well as carburizing agents [55]. The composition and dispersion of Mo and C in the structures vary influencing the electrochemical activity. Further, the structures exhibit varying sizes of the tunnel, which affects ions insertion. The crystal structure of α-Mo₂C is fcc, which is similar to that of NaCl while both γ-MoC and η-MoC exhibit hexagonal structures but different stacking sequence [54]. According to the Joint Committee on Powder Diffraction Standards (JCPDS) data files, β-Mo₂C is orthorhombic with the Mo arrangement slightly distorted from hcp [51], while α-Mo₂C has hcp surface with carbon atoms incorporated at the octahedral interstitial sites [55]. Both of them are suitable for hydrogenation of CO [5,56] and conversion of benzene to cyclohexane [57]. However, the orthorhombic β-Mo₂C is more stable while the hexagonal α-Mo₂C is less stable [58]. Fig. 7 presents the Bulk crystallographic structures of MCN.

Prominent of all the MCN structures are α-Mo₂C, β-Mo₂C [24,60] due to their high stability and remarkable electrochemical performance, which is attributable to their large ionic contribution [55]. Further, β-Mo₂C is a suitable electrocatalytic material due to its low work function (3.4 eV), which facilitates surface-adsortbate electron transfer [55]. Based on DFT computation, β-Mo₂C exhibits a stronger metallic property than the other polymorphs, which show the strongest covalent bond [55]. The lattice constant computed using DFT-RPBE for bulk α-Mo₂C is 4.36 Å [61,62] while the experimental value is 4.33 Å [63]. The β-Mo₂C comprises a sequence of alternating Mo and C layers with DFT-RPBE lattice constants: a = 4.819 Å, b = 6.012 Å, and c = 5.150 Å [61,62], which are similar to the obtained experimental data by [64]. The lattice constant of computed for α-Mo₂C are: a = b = 6.118 Å and c = 4.682 Å [46], which are reportedly close to the experimental values [65]. All the strategies for MCN preparation are related to reductive carburization of the precursor material in a stream containing hydrogen via TPH [66], and chemical vapor deposition (CVD) [67], liquid-phase reaction [68], template method [69], etc. Prominent of all the strategies is TPH, which involves a reductive reaction between the hydrogen, carbon source (light hydrocarbon) and the Mo precursor. To obtain β-Mo₂C with an enhanced number of active sites, in situ carburization is vital. This constructs β-Mo₂C nanoparticles with a fast electron transfer path, which could be covalently anchored on a promoter [70]. The reaction scheme is given in Fig. 8.

Due to all these outstanding qualities of MCNs, β-Mo₂C was proposed as a viable substitute for the conventional Cu-based catalysts utilized in reactions like Water-Gas-Shift (WGS) [71,72] while α-Mo₂C highly suitable for dehydrogenation of ammonia [73].

4. Surface properties of MCNs

MCNs possess a similar surface to that of transition metal surface M (111), which is a little more reactive toward CH₂/₃ species when compared with metals with a similar strength of carbon adsorption. This makes MCN a suitable for hydrogenation reaction, which is less vulnerable to graphite poisoning because of an increased attraction to hydrocarbons [74]. Moreover, Mo₂C (001) has a similar the O/OHx binding with that of the transition metal M(211) surfaces indicating the likelihood of oxygen poisoning on Mo₂C surfaces. However, if there is deposition of oxygen from the decomposition of CO₂ or water, the Mo₂C surface becomes stable against subsurface oxidation, while for oxygen deposition from methanation of CO, a subsurface oxycarbide is
expected to be stable at low temperatures and lower kinetic rate as compared with carbon dioxide or water decomposition [74]. The suitability of MCNs for hydrogenation reaction is also supported by the outcome of the study of Posada-Perez et al. [45], which concluded that MCN is an active and selective catalyst for CO2 reduction to methanol. This is because adsorption and decomposition of CO2 are more effective on the surface of Mo-terminated β-Mo2C(0001) compared to transition metal surfaces like Cu(111) being the surface that is generally used as a standard in catalysis [75]. Posada-Perez et al. [45] stated that the apparent activation energy obtained for the synthesis of CH3OH via CO2 reduction on MoC is 17.2 kcal mol\(^{-1}\), which is lower than the respective values of 25.4 and 20.9 kcal mol\(^{-1}\) reported for Cu(111) and TiC(001) [76].

Several studies show that the structure of Mo2C surface depends on the annealing time and temperature [77–80]. The study of Lo et al. [77] reveals that the three-fold hollow sites of Mo layer were occupied by the C atoms when annealed below 687 °C when high-resolution images of Mo2C(0001)-(\(\sqrt{3} \times \sqrt{3})R30°\) structure were investigated by scanning tunneling microscopy. Fig. 9 presents the low Miller-index surfaces of fcc α-Mo2C, hexagonal MoC, α-Mo2C and β-Mo2C. The α-MoC(111) was structured in a way that Mo and C-terminated (111) planes. The (001) surface is found to be the most stable while (011) surface is unstable. The hexagonal MoC phase, which is obtained with an annealing temperature of 1327 °C [79] possesses (001) and (100) polar surfaces with both Mo- and C-terminated (Fig. 10).

Both α-Mo2C and β-Mo2C have Mo- and C-terminated polar surfaces ((001) and (111)) when annealed above 1027 °C and nonpolar (100), (011), and (101) [78]. The atomic sites were completely relaxed in all the slab super-cell models even though neither the variations in surface energies nor the surface reconstruction was amongst the engaged super-cells [55].

The surface stability of MCNs are not only determined by the surface structures but also operating conditions like carburization process, and (b) XRD pattern showing the crystalline phases of the synthesized MCN. Recognized crystalline phase: (□) Mo2C, Mo, and (X) MoO2; adopted from [20].

5. Multiscale reaction model on MCNs

For a better understanding of catalytic reaction mechanism with MCNs, there is a need to establish a multiscale reaction model, which combines quantum mechanical (QM) density functional tight-binding (DFTB) technique with a molecular mechanical (MM) force field [82,83]. This could be accomplished by building a QM/MM model to define the MCN, the model aromatic solvent, and the surroundings. The free energy profiles of the reactions could be determined by using Umbrella sampling (US) [82]. Liu and Salahub [82] studied a multiscale reaction model of a catalytic hydrogenation of benzene on MCN by using QM/MM method together with US technique towards in situ upgrading of heavy oil. Their report shows that the multiscale model reveals new features of MCN as compared with the traditional computational method. Consequently, the MCN and the solvent made entropic contributions, which significantly influence the free energy profiles of the nanoscale heterogeneous reactions to establish a reaction working condition. Fig. 9 gives the optimized embedded reactant state of the first hydrogenation reaction.

However, the multiscale model efficiency is determined by the cost of computation on ab initio. It is of vital importance to search for a more economical means for large-scale simulation using ab initio molecular dynamics [84]. Functional forms such as bond-order based potentials suggested by Brenner and Garrison [85] and Tersoff [86] for covalent materials, embedded atom type (EAM) potentials for metals [87], and classical force fields [88] for molecular systems has been recommended. However, they are all limited in numerical accuracy and inability to reuse the functional form for another system order than the particular system for which it was modeled [89]. Further, several approaches based on electronic data fitting such as splines [90], Gaussian approximation potentials [91], modified Sheppard interpolation (MSI) based on a Taylor expansion [92], genetic programming [93], reproducing kernel Hilbert space (RKHS) [94], expansion in terms of invariant polynomials (IP) [95] and interpolating moving least squares (IMLS) [96] have been suggested. Although these approaches are
exceptionally and perfectly numerical, the functional form is “non-
physical” (bias-free). Therefore, the construction of the PESs needs to
be greatly done to give the appropriate physical representation
of the system [89].

Recently, the use of neural-network (NN) as an intelligence tech-
nique to represent the ab initio potential energy surface (PES) adap-
tively is a promising approach. NN offers a remarkable computational
efficiency and is capable of reproducing the experimental data thereby
giving an exceptionally cheap and quality model of the physico-
chemical process [97]. Neural-network is a class of algorithms formulated for
various applications [89]. Among them are applications related to PES
such as estimation of the correlation energy of heavy atoms and dia-
tomic molecules [98], modeling of bond energies [99], enhanced en-
thalpies [100,101] and heat of formation [102], and lower level elec-
tronic structure-based computation of DFT energies [103]. The
applications ride on the capability of NNs to discover a hidden pattern
in complex data [89]. According to the study of Behler [89], NNs o
ffer several advantages compared to the conventional potential. The ad-
vantages include accuracy, improvability, efficiency, cost-effectiveness,
lack of system specific terms, the ability to deal with high dimensional
PESs and ability to analyze how bonds are broken and made. Further-
more, the construction is highly automatic with little human e
ffort. The
potential constructed for a specific system can be used to predict the
energies of atomic configurations of related structures in the training
set. In addition, the analytic gradients are readily available due to their
well-de
fi
ned functional form. The recent study of Artrith and Behler
[104] on the properties of bulk copper and of a variety of surface
structures reveals that NN PESs have the capacity to produce a similar
result with that DFT at a small fraction of the computational costs.

NN PESs could be constructed via several approaches, which include
single NN, systematic NN potentials, and high-dimensional NN poten-
tials. Single NN PESs can be trained implemented with ease and the
potentials could be evaluated speedily and accurately. However, they
are only applicable to small molecules because the potentials are lim-
ited to low degree of freedom. PESs based on systematic NN potentials
are suitable for large molecule [105,106] and serve as an intermediate
to high-dimensional NN potentials. High-dimensional NNS normally

![Fig. 5. (a) Production rates of methanol from CO₂ hydrogenation on β-
Mo₂C(001)-Mo and polycrystalline MoC at 500 and 600 K and Arrhenius plots
for the production of (b) CO, methane and methanol on β-Mo₂C(001)-Mo; (c)
CO and methanol on MoC at temperatures of 600, 575, 550, 525, and 500 K. In
a batch reactor, the metal carbide catalyst operating at 0.049 MPa (0.5 atm) of
CO₂ and 0.441 MPa (4.5 atm) of H₂; adopted from [48].](image1)

![Fig. 6. TPH profiles of the MCN before (A) and after (B) CO hydrogenation
reaction at m/z = 15 adopted from [39].](image2)
suitable for huge systems comprising some thousands of atoms [89]. According to the study of Behler [89], an ideal potential should be high-dimensional and obviously determined by using the entire degree of freedom of the system with a reliable set of high-level ab initio data. It could be used for a variety of systems without changes in their functional form, and a remarkable accuracy close to the fundamental first-principles molecular dynamics simulations is achievable because of their bias-free construction [107,108]. Sosso et al. [109] even suggested that the capability of NN PES is beyond that of the first-principles. This was observed when they used NN techniques to develop a classical interatomic potential for the bulk phases of GeTe.

However, high-dimensional NN potential is more costly. They are capable of providing energies and forces from 100 to 200 atoms per second per computation core on average desktop computers, although it is by far faster than DFT [110]. Since NN PESs need bigger training sets compared to other kinds of potentials for an adequate description of the physics of the system, it is mandatory to consider the required equilibrium structures as well as non-stationary points in the training set to avoid holes in high-dimensional NN PESs. However, the training data set should be minimized to reduce computational cost, since only the energetically reachable part of the data set such as the configurations visited in MD simulations are significant [89].

Shen et al. [83] studied a multiscale model towards lowering the cost of ab initio computation by using NN as proposed by Behler and Parrinello [110]. They developed a semi-empirical QM/MM model for determination of potential energy of a specific QM/MM system at ab initio QM/MM level. The developed model was further utilized for three more reactions in water to estimate the changes in free-energy. The ab initio QM/MM level was obtained by converting the semi-empirical QM/MM model computed free-energy profile with the potential energies predicted with the developed NN. The obtained results show a remarkable correlation with the reference data gotten from the ab initio QM/MM molecular dynamics model [83]. This shows that application of NN method couple with semiempirical QM/MM model is an efficient and reliable approach for modeling of a chemical reaction. The previous study of Nguyen-Truong et al. [111] also attested to the efficacy of NN by using Levenberg–Marquardt (LM). They revealed that the algorithm is exhibited high accurate with less training iterations and the fitting (vibrational PES of H2O, reactive PESs of O3 and ClOOC) require fewer data points.

However, the use of NN is becoming an old fashion due to the emergence of a simpler, more cost-sensitive and efficient learning approach known as extreme learning machine (ELM) developed by Huang et al. [112]. This is because ELM exhibits extremely fast learning speed, superior suitability for high-dimensional potentials, and generalization capability. ELM is a learning algorithm for single-hidden layer feed-forward neural networks (SLFNs), which selects hidden nodes randomly and computes the output weights of SLFNs analytically. ELM can be regarded as a linear system after the input weights and the hidden layer

**Fig. 7.** Bulk crystallographic structures of (a) fcc $\alpha$-MoC$_{1-x}$, (b) hexagonal $\gamma$-MoC and $\eta$-MoC, and (c) orthorhombic $\beta$-Mo$_2$C. Turquoise and magenta spheres denote C and Mo atoms, respectively adopted from [57].

**Fig. 8.** Reaction scheme for Mo2C formation via in situ carburization using Temperature program hydrogen (TPH).

**Fig. 9.** Top (left panels) and side views (right or middle panels) of the considered $\alpha$-MoC$_{1-x}$, hexagonal MoC, and $\alpha$-Mo$_2$C & $\beta$-Mo$_2$C surfaces. In the $\alpha$-MoC$_{1-x}$ (111) surfaces three panels are presented, being Mo- (left panel) and C-terminations (right panel). On $\alpha$-Mo$_2$C & $\beta$-Mo$_2$C polar surfaces—(111) and (001)—left and right panels belong to C- and Mo-terminations whereas the middle panel is a top view. Surface unit cells are appeared as red lines; adopted from [57]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
bias are randomly selected \[\text{[113]}\]. Being one of the foremost trends for optimization and high learning speed in the machine intelligence community, ELM has a promising potential to scale up for several practical applications, while attaining the developments in theories, applications, and hardware implementation \[\text{[113,114]}\].

By using ELM, the neural networks training time can be lessened by a thousand times. The performance of ELM has been assessed on several benchmark problems \[\text{[115]}\]. However, ELM PESs not been investigated to the best of our knowledge.

6. Application of MCN for hydrogenation and hydrogen production

6.1. Unsupported MCN

Recently, Posada-Pérez et al. \[\text{[116]}\] reported the use of MCN heterogeneously catalyzed hydrogenation reactions, where \(\text{H}_2\) is adsorbed and dissociated. The study was carried out using systemic DFT-PBE with or without dispersion terms, regarding the interaction and stability of \(\text{H}_2\) with orthorhombic \(\beta\)-Mo\(_2\)C(001) and cubic \(\delta\)-MoC(001) surfaces. For \(\beta\)-Mo\(_2\)C(001), two likely Mo or C terminations are considered. Their report shows that the energy profiles for the elementary steps \(\text{H}_2\) dissociation are mainly influenced by dispersion. The DFT-PBE computation with vdW dispersion give an energy barrier of 0.60 eV for \(\text{H}_2\) dissociation and adsorption. The study was carried out using systemic DFT-PBE for dehydrogenation of benzyl alcohol to benzaldehyde. Their report shows that the catalytic performance of the catalysts on MCN during catalytic hydrogenation of CO to produce mixed aliphatic mesoporous carbon (GMC), carbon black and activated charcoal) \(\beta\)-Mo\(_2\)C, while it was predicted that \(\delta\)-MoC and \(\beta\)-C become more than dissociation. The computation of surface free energy calculations indicates that both terminations of \(\beta\)-Mo\(_2\)C become stable as H coverage increases. On the other hand, in the case of the \(\delta\)-MoC (001) surface, adsorption of H becomes stable up to half coverage where all C sites are filled (Table 1).

Li et al. \[\text{[36]}\] developed belt-shaped MCN (\(\alpha\)-Mo\(_3\)C\(_1\_x\) and \(\beta\)-Mo\(_2\)C) for dehydrogenation of benzyl alcohol to benzaldehyde. Their report shows that \(\beta\)-Mo\(_2\)C nanobelts displayed a higher catalytic performance than the \(\alpha\)-Mo\(_3\)C\(_1\_x\). The outstanding performance of \(\beta\)-Mo\(_2\)C could be attributed to the high number of coordinatively unsaturated Mo sites on its surface. The study of T. Mo et al. \[\text{[43]}\] on hydrogenation of CO, states that increase in the degree of carburization weakens the CO adsorption strength on MCN. However, increase in degree carburization of MCN engenders a continuous increase in the intrinsic activity with respect to TOF. Table 2 presents the catalytic performance of various unsupported MCN catalysts.

6.2. Supported MCN

Several authors have studied supported MCN for the purpose of establishing selectivity control in reactions such as HDO. Boullosa-Eiras et al. \[\text{[120]}\] studied the use of \(\text{TiO}_2\) supported MCN (Mo\(_2\)C/\(\text{TiO}_2\)) as an alternative catalyst for HDO of fast pyrolysis of phenol as a bio-oil model compound. The reaction was performed at a temperature range of 350–450 °C at a pressure of 25 bar. The primary product obtained is benzene (large amount) via hydrogenolysis, indicating high selectivity towards benzene. Small quantities of non-aromatics such as methyleclopentane, cyclohexene, and cyclohexane were also observed. The best catalytic performance was obtained at 350 °C and 25 bar with a moderate deactivation after 9 h on stream.

MCN supported platinum (Pt/Mo\(_2\)C) catalysts was successfully used for water gas shift (WGS) reaction, exhibiting a remarkable WGS rate (mol CO/molPt s), which is better than the rates reported for commercial Cu-Zn-Al catalyst and most of the active oxide supported Pt catalysts (like Pt/\(\text{CeO}_2\), Pt/\(\text{CeO}_x\), and Pt/\(\text{TiO}_2\)) \[\text{[117]}\].

Zou et al. \[\text{[122]}\] investigated the effect of various additives such as K, Ce, Co, Mg and La on MCN supported on Ni impregnated \(\gamma\)-\(\text{Al}_2\)\(_2\)O\(_3\) during tri-reforming of methane. Their report shows that the presence of Ni species stirred-up methane dissociation and made active carbon available for the carburization process. Addition of La to the Ni supported MCN is capable of preventing small particles aggregation, facilitating topotactic transformation of MCN species and suppressed deposition of carbon, thereby leading to remarkable catalytic performance. Addition of Ce and Co resulted in deterioration of the activities of the catalyst to some extent because the particle size is larger, while the addition of Mg decreased the porosity of the catalyst and promoted coke formation. The addition of K inhibited the carburization process of molybdenum oxide species and caused the phase transformation of active \(\gamma\)-\(\text{Al}_2\)\(_2\)O\(_3\) to less active \(\theta\)-\(\text{Al}_2\)\(_2\)O\(_3\). K and Mg-promoted Ni supported MCN, particularly the former, displayed a dramatic decline in the redox ability for the methane tri-reforming.

Chai et al. \[\text{[123]}\] studied the effect of various carbon support (graphitic mesoporous carbon (GMC), carbon black and activated charcoal) on MCN during catalytic hydrogenation of CO to produce mixed alcohol. Their report shows that the catalytic performance of the catalysts on MCN particle size rather than the type of support (Table 3). Consequently, GMC was observed as the most promising support of \(\beta\)-Mo\(_2\)C due to its ability to form smaller carbide particles leading to higher catalytic performance. Incorporation of a small amount of \(\text{K}_2\)\(_2\)CO\(_3\) into \(\beta\)-Mo\(_2\)C/GMC (molar K/Mo = 0.05–0.5) as a promoter considerably favors the production of C\(_2\)+\(-\text{OH}\), resulting in a maximum space time yield (STY) for C\(_2\)+\(-\text{OH}\) at medium K/Mo ratio of 0.1. \(\text{K}_2\)\(_2\)CO\(_3\) promoted \(\beta\)-Mo\(_2\)C/GMC exhibited a better C\(_2\)+\(-\text{OH}\) selectivity and space-time yield (STY) when compared with a typical Rh/GMC catalyst when triply promoted with oxide of Fe, Li, and Mn.

Kiai et al. \[\text{[124]}\] prepared a series of carbon nanotubes (CNTs)
The enhanced selectivity of higher alcohols may be upon incorporation of K, thereby favoring formation of alcohol. When catalysts are more effective and function at a superior rate, thereby saving time, exhibits better rate than commercial Cu-Zn-Al catalyst and most of the active oxide supported catalysts. Although the supporter saves time, exhibits better rate than commercial Cu-Zn-Al catalyst and most of the active oxide supported catalysts. Although the incorporation of the support could incur extra cost of material and process, but the additional cost is worthwhile since supported MCN catalysts are more effective and function at a superior rate, thereby saving time and lowering the cost of using the catalyst for sustainable energy production.

6.3. oxygen-modified molybdenum carbide catalysts

MCN being an oxophilic catalytic materials from both a...
Catalytic performance of various unsupported MCN catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Reaction</th>
<th>T (K)/ P (MPa)</th>
<th>Performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MoCl₁₋ₓ</td>
<td>71.6/2.2²</td>
<td></td>
<td>dehydrogenation</td>
<td>393/ –</td>
<td>80⁴</td>
<td>[36]</td>
</tr>
<tr>
<td>β-MoO₃</td>
<td>88.9/2.3³</td>
<td></td>
<td>dehydrogenation</td>
<td>393/ –</td>
<td>100³</td>
<td>[36]</td>
</tr>
<tr>
<td>Mo₅S₅0</td>
<td>45.7/ –</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>553/3.1</td>
<td>0.07¹</td>
<td>[43]</td>
</tr>
<tr>
<td>Mo₆O₃₃</td>
<td>22.1/ –</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>553/3.1</td>
<td>0.07⁴</td>
<td>[43]</td>
</tr>
<tr>
<td>Mo₇O₇0</td>
<td>20.7/ –</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>553/3.1</td>
<td>0.078⁵</td>
<td>[43]</td>
</tr>
<tr>
<td>Mo₈O₈0</td>
<td>27.1/ –</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>553/3.1</td>
<td>0.081¹</td>
<td>[43]</td>
</tr>
<tr>
<td>Mo₉O₉0</td>
<td>15/-</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>473/4</td>
<td>69¹</td>
<td>[117]</td>
</tr>
<tr>
<td>α-MoC₁ₓ ᵧ –</td>
<td>–</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>473/2</td>
<td>74¹</td>
<td>[117]</td>
</tr>
<tr>
<td>β-Mo₂C</td>
<td>–</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>473/2</td>
<td>29¹</td>
<td>[118]</td>
</tr>
<tr>
<td>Mo₂C</td>
<td>–</td>
<td></td>
<td>Hydrogenation of CO</td>
<td>473/6</td>
<td>32.4¹</td>
<td>[119]</td>
</tr>
</tbody>
</table>

¹ TOF (s⁻¹).  
² Conversion (%).  
³ Selectivity of ROH.

Table 3
Catalytic performance of various promoted/supported MCN catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Particle size (nm)</th>
<th>Reaction</th>
<th>T (K)/P (MPa)</th>
<th>Performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 MoO₃/TiO₂</td>
<td>65/-</td>
<td></td>
<td>22</td>
<td>HDO</td>
<td>623/2.5</td>
<td>0.003⁴</td>
<td>[120]</td>
</tr>
<tr>
<td>15 Mo₅S₅₀/TiO₂</td>
<td>66/-</td>
<td></td>
<td>24</td>
<td>HDO</td>
<td>623/2.5</td>
<td>0.009²</td>
<td>[120]</td>
</tr>
<tr>
<td>6.8 Mo₅₃₀/TiO₂</td>
<td>74/-</td>
<td></td>
<td>11</td>
<td>HDO</td>
<td>623/2.5</td>
<td>0.003⁶</td>
<td>[120]</td>
</tr>
<tr>
<td>PtMo₂C</td>
<td>–</td>
<td></td>
<td>–</td>
<td>Water Gas Shift</td>
<td>513/-</td>
<td>1.42³</td>
<td>[121]</td>
</tr>
<tr>
<td>NiMo₃₅₀-La</td>
<td>142.68/7.31</td>
<td></td>
<td>–</td>
<td>methane tri-reforming</td>
<td>1523/-</td>
<td>93.95⁵</td>
<td>[122]</td>
</tr>
<tr>
<td>NiMo₃₅₀-Mg</td>
<td>119.51/6.94</td>
<td></td>
<td>–</td>
<td>methane tri-reforming</td>
<td>1523/-</td>
<td>96.05⁶</td>
<td>[122]</td>
</tr>
<tr>
<td>NiMo₃₅₀-K</td>
<td>103.67/6.24</td>
<td></td>
<td>–</td>
<td>methane tri-reforming</td>
<td>1523/-</td>
<td>7.32²</td>
<td>[122]</td>
</tr>
<tr>
<td>NiMo₃₅₀-Co</td>
<td>129.53/7.42</td>
<td></td>
<td>–</td>
<td>methane tri-reforming</td>
<td>1523/-</td>
<td>99.30²</td>
<td>[122]</td>
</tr>
<tr>
<td>NiMo₃₅₀-Ce</td>
<td>132.32/7.28</td>
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<td>–</td>
<td>methane tri-reforming</td>
<td>1523/-</td>
<td>98.60º</td>
<td>[120]</td>
</tr>
<tr>
<td>Co/MoC</td>
<td>–</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>603/3.3</td>
<td>4.8⁸</td>
<td>[14]</td>
</tr>
<tr>
<td>0.2K/Co/MoC</td>
<td>112/13.12</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>603/3.3</td>
<td>42.2⁹</td>
<td>[124]</td>
</tr>
<tr>
<td>0.4K/Co/MoC</td>
<td>101/13.39</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>603/3.3</td>
<td>44.6⁴</td>
<td>[124]</td>
</tr>
<tr>
<td>0.6K/Co/MoC</td>
<td>88/13.53</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>603/3.3</td>
<td>48.3⁴</td>
<td>[124]</td>
</tr>
<tr>
<td>0.8K/Co/MoC</td>
<td>72/13.76</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>603/3.3</td>
<td>41.3³</td>
<td>[124]</td>
</tr>
<tr>
<td>K/β-Mo₂C/GMC</td>
<td>–</td>
<td>10.8 ± 6.3</td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>573/3.0</td>
<td>29.5, 7º</td>
<td>[123]</td>
</tr>
<tr>
<td>β-Mo₂C/AC</td>
<td>95/1 &lt; 2.0</td>
<td>14.3 ± 3.1</td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>573/3.0</td>
<td>29.5, 15³</td>
<td>[123]</td>
</tr>
<tr>
<td>Rb-MnLi·Fe/GMC</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>573/3.0</td>
<td>24.5, 46º</td>
<td>[123]</td>
</tr>
<tr>
<td>Mo₅C</td>
<td>151</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>473/4</td>
<td>69²</td>
<td>[113]</td>
</tr>
<tr>
<td>Cu/Mo₂C</td>
<td>135</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>473/4</td>
<td>76²</td>
<td>[117]</td>
</tr>
<tr>
<td>α-MoC₁ₓ ₀.₈ –</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>473/2</td>
<td>74³</td>
<td>[117]</td>
</tr>
<tr>
<td>β-Mo₂C</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>473/2</td>
<td>29³</td>
<td>[118]</td>
</tr>
<tr>
<td>Co/Mo₂C</td>
<td>135</td>
<td></td>
<td>–</td>
<td>Hydrogenation of CO</td>
<td>493/6</td>
<td>22³</td>
<td>[118]</td>
</tr>
</tbody>
</table>

15 Mo₂C/TiO₂ = Mo₂C/TiO₂ with ca. 15 wt% of Mo loadings.

¹ TOF (s⁻¹).  
² Water Gas Shift (mol CO / molPt).  
³ H₂ yield at a feed flow rate of 4600 mL h⁻¹.  
⁴ Selectivity of ROH at varying K/Co molar ratio (from 0.2 to 0.8) and MoCo = 1.66.  
⁵ 1 wt% Rh, Rh/Mn/Li/Fe = 1/1.9/1/1/0.1.  
⁶ C₂+—OH Selectivity (mol-C%, CO₂-free), Space time yield (mg (h gcat)⁻¹).  
⁷ 5 wt% β-Mo₂C, K/Mo = 0.1.
**Table 4**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Trxn (K)</th>
<th>CO2 conv. rate/TOF</th>
<th>Selectivity (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µmol/mmol s^-1</td>
<td>s^-1 10&lt;sup&gt;1&lt;/sup&gt;</td>
<td>MeOH EtOH CO CH4 C2H4 C2H6 C3+</td>
<td></td>
</tr>
<tr>
<td>Mo2C</td>
<td>408</td>
<td>1.7</td>
<td>0.6</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>55</td>
<td>20</td>
<td>53</td>
</tr>
<tr>
<td>Cu/Mo2C</td>
<td>408</td>
<td>4.6</td>
<td>2.1</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>90</td>
<td>41</td>
<td>63</td>
</tr>
<tr>
<td>Pd/Mo2C</td>
<td>408</td>
<td>5.9</td>
<td>2.3</td>
<td>95</td>
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<td></td>
<td>473</td>
<td>97</td>
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<tr>
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<td>408</td>
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<td>1.9</td>
<td>84</td>
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<td>473</td>
<td>86</td>
<td>35</td>
<td>46</td>
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<tr>
<td>Fe/Mo2C</td>
<td>408</td>
<td>3.9</td>
<td>1.5</td>
<td>87</td>
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<tr>
<td></td>
<td>473</td>
<td>99</td>
<td>38</td>
<td>58</td>
</tr>
</tbody>
</table>

<sup>a</sup> 10 bar CO2, 30 bar H2, 37.5 mL 1,4-dioxane and 200 mg catalyst.

<sup>b</sup> Calculated at 2h.

<sup>c</sup> Calculated at ~ 1.0% CO2 conversion at 135 °C and ~ 10% CO2 conversion at 200 °C. The selectivities were calculated on a C1 basis.

<sup>d</sup> C3 contains C3H6 and C3H8, and C4 contains C4H6 and C4H10.
promoter. Addition of support/promoter enhanced the catalytic performance of 


