Utilization of structural high entropy alloy for CO oxidation to CO₂

Anjali Sharmaa†, Nirmal Kumar Katiyarb,c†, Arko Paruird†, Rakesh Das, Abhishek Kumar Singhd*, Chandra Sekhar Tiwarye*, Sudhanshu Sharmaa*, Krishanu Biswasb*

department of Chemistry, Indian Institute of Technology Gandhinagar, Gandhinagar 382355, India
bDepartment of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India
cSchool of Engineering, London South Bank University London, 103 Borough road, London SE10AA
dMaterials Research Centre, Indian Institute of Science, Bangalore 560012, India
eMetallurgical and Materials Engineering, Indian Institute of Technology Kharagpur, Kharagpur 382355, India
*Corresponding authors, Email: abhishek@iisc.ac.in, ssharma@iitgn.ac.in, Chandra.tiwary@metal.iitkgp.ac, kbiswas@iitk.ac.in
†Equal Contribution

Abstract

The nanoengineered high entropy alloy (HEAs) catalysts have attracted the attention of the scientific community due to their exceptional characteristics; wide range of compositional tunability and the utilization of low-cost transition metals. During various electrochemical reactions, the oxidation of carbon-mono-oxide (CO) is an intermediate and it acts as a poison to reduce the efficiency of the reactions. A nanocrystalline HEA catalyst (CoFeNiGaZn) is prepared by easily scalable cast-cum-crush method, providing pristine catalyst surfaces. It is capable of catalyzing the CO-oxidation to CO₂ with high conversion efficiency (99.8%). DFT calculations show that the high activity of the HEA can be attributed to the presence of a considerable amount of filled states of $d_{xz}$ and $d_{yz}$ orbital near the Fermi level for Ni atoms over the surface. Due to the favourable transfer of electrons from this orbital to the LUMO of reactant molecules, the endothermicity of the rate-determining step is 1.13 eV.

Keywords: Electro-oxidation; High entropy alloy, Catalyst, Low cost, DFT, Transition metals
The engineered nano or atomic scale catalysts have revolutionized the domain of catalysis by providing high selectivity and activity with long term stability, raising hope for sustainability for industrials applications [1, 2]. However, noble metal catalysts, commonly utilized are too precious to make them viable for commercial operation. Therefore, nanoengineered catalysts using low-cost elements (transition metal elements), which must be endowed with high stability and efficiency, are the need of the hour. In this regard, different types of materials are under active consideration as well as investigation, revolutionizing the catalytic science to meet the novel requirements, including graphene for HER reaction [3], electronic waste as a catalyst for water splitting[4], carbon dots for ORR and OER reactions [5] etc. However, limitations exist, such as the yield of the catalyst preparation, lack of efficiency, and lower selectivity, which requires the design and development of new catalysts

A new concept called entropy stabilized multicomponent alloys, popularly known as high entropy alloys has emerged and reported to be successful in design of novel catalysts for variety of reactions [6]. The five or more elements are mixed in equiatomic or near equiatomic ratio to form single-phase alloys, which has recently been used to design novel catalysts [7, 8]. They have shown tremendous potential due to their vast compositional space comprising almost all the metallic elements in the periodic table, allowing us to tune the chemistry and surface microstructure and provide the unlimited scope of design new multipurpose catalysts. Among the low-cost metals available in the periodic table, the alloys made of 3d-transition metals (TMs) are considered to be the best candidates for the nanoengineered HEA catalysts [6]. The four-core effects of HEAs impart exceptional properties; high entropy providing the single-phase stabilization, sluggish diffusion imparting long-term stability, cocktail effect altering their d-band centre with respect to Fermi energy level, and the lattice distortion modifying energy levels of
free electrons[9-11]. Therefore, the high entropy alloys (HEAs) are expected to provide an active catalyst because a single-compositional alloy can exhibit multiple reactions due to multi-elemental bonds dangling over the surface with a unique surface electronic structure favourable for the adsorption[12]. This allows the design gamut of the chemistry of high entropy catalysts with different elements for their electrochemical responses. This includes degradation of azo dyes using AlCoCrTiZn HEA catalyst[13], converting CO₂ into highly reduced hydrocarbon (CH₄, CH₃OH) using AgAuPdPtCu HEA catalyst [14], formic acid and methanol to hydrogen fuel[15]. The NH₃ decomposition using high entropy alloy (CoMoFeNiCu) was 20 times higher than the pure Ru catalyst[16]. CO oxidation reaction, one of the important yet simple exhaust treatment reactions, has not extensively been studied on the high entropy catalysts. Preferential CO oxidation is important to purify hydrogen gas where CO concentration of lower than 5 ppm is required [17]. Supported Pt catalyst is the most widely used one for this reaction although the cobalt-based catalysts exist, providing ultra-low temperature activity [18, 19]. Among various materials used for this reaction are supported metal oxides, perovskite, spinels, substituted metal oxides etc [20-23]. Among the emerging class of materials, HEAs can possibly outperform previously known catalysts for CO oxidation reaction. However, the magic chemistry is still unknown as a low volume of work exists for CO oxidation reaction on HEAs [24]. In fact, a basic kinetic investigation is not reported so far, which can, in principle lead to a fair comparison of HEAs with the conventional catalysts. In this work, we have explored the CO oxidation activity on low cost easily scalable CoFeZnNiGa HEA nanoparticles. The kinetic parameters have been estimated and compared with the other known catalysts in the literature. The nanocrystalline CoFeZnNiGa HEAs has been prepared by the method of cast-and-crushing, involving cryomilling of the cast alloy ingot at extremely low temperature [25, 26]. Therefore,
the surface of the catalyst remains native or uncapped due to low temperature milling, making it viable for catalytic applications [25, 27]. Further DFT calculations were done to find the active site over the HEA surface along with the probable mechanism, where mainly the effect of suitable orbital overlap among the HEA and reactant molecule was considered.

**Results and discussion**

Figure 1(a) shows the schematic representation of the recipe of synthesis and nature of atomic arrangement on the HEA nanoparticle; each constituent of HEA is present on surface of the nanoparticle, allowing adsorbate molecule to land over the surface of the nanoparticles and turn to CO$_2$. A unique recipe has been applied to prepare a five-element HEA catalyst using low-cost materials transition elements for this purpose; Fe, Ni, Co, Ga and Zn. The elements were melted together in an argon environment to obtain an ingot and then milled at extremely low temperatures (-123 K) to avoid oxidation and contamination of the nanocrystalline HEA. The XRD pattern (Figure 1b) reveals single-phase FCC nanoparticles are being synthesized by this route. The size and shape of as-prepared nanoparticles were obtained from bright-field TEM micrograph (Figure 1(c)) and the average size is found to be $\sim$12 ±3 nm. Their surface is pristine, as shown in the HRTEM image of a nanoparticle in Figure (d). It is to be noted that there are five different elements in single HEA nanoparticle, and therefore, the homogeneity (element distribution) has been confirmed by elemental mapping using EDS attached to the TEM. Figure 1(f) shows elemental maps for a nanoparticle, revealing that all elements are homogeneously distributed in the single-phase materials.
The HEA nanoparticles are further investigated for heterogeneous gas-solid reaction in the unsupported state. The CO-oxidation reaction is carried out under stoichiometry conditions, the details of gas mixture containing 10% carbon monoxide, 10% Oxygen and remaining Nitrogen. The conversion profile of CO over CoFeZnNiGa as a function of the temperature is shown in Figure 2(a). All profiles are recorded in the temperature range from room temperature to 400 °C and using the CO/O₂ ratio of 2:1.
Figure 2: (a) Percentage CO conversions of CO + O₂ reaction at different GHSV for CoFeZnNiGa, (b) Percentage CO Conversion vs W/F at 313K, 348K and 373K for different GHSV (descending from left to right) at atmospheric pressure. The amount of the catalyst for all cases is fixed at 55 mg, (c) Arrhenius plot for CO+O₂ reaction over CoFeZnNiGa catalyst. The reported values are for steady-state rates measured at temperatures of 313, 348, and 373K with a total conversion of CO below 12%, (d) Activation energy for different catalyst materials of CO oxidation reaction (data collected from the literature).

The dependence of CO conversion on the flow rates was studied and the results are shown in Figure 2(b). As the space velocity was increased from 10,000 – 40,000 h⁻¹ (GHSV), no effect was observed on the CO conversion profile and temperature. It concludes that external diffusion (mass transfer) has a limited role on the catalytic activity. This is partially due to the fact that
HEA nanoparticles do not contain any macroscopic porosity (as its free-standing nature). Maximum % conversion of CO over CoFeZnNiGa was found out to be 99.8% at 175°C at 10,000 h⁻¹ GHSV. The rate of CO oxidation reaction was also calculated at various temperatures from the slope of the curve \((W/F)\) with the molar conversion of CO (Figure 2c). Here, \(W\) is the weight of the catalyst, and \(F\) is the flow rate of CO in sccm [19, 28, 29]. Rates of the reaction w.r.t. weight at temperatures 313K, 348K, 373K were found out to be 2.38, 5.26, 6.39 µmol/g/sec, respectively. Activation energy was found to be 3.761 kJ/mol, which is the lowest among the materials well-known in literature (Figure 2d). Clearly, the HEA catalyst is highly active for the CO oxidation reaction.

To shed light on the probable mechanism and active sites for reaction, density functional theory (DFT) calculations were performed. In the first step, FCC bulk structure of Ni was taken from Materials Project [30] to generate the FCC-HEA surface. Optimized lattice parameters are (a=b=c=3.52 Å) which is in good agreement with previous report [31]. The (111) facet was selected for DFT calculations, as it shows the most prominent pick in the XRD pattern. It was generally believed that for CO oxidation (CO + O\(\rightarrow\)CO₂), O₂ adsorption takes place on the surface. Its dissociation follows this on transition metals as O₂ can easily dissociate on all transition metals at room temperature[32]. Therefore, the reaction follows Langmuir-Hinshelwood mechanism, and the elementary steps involved in the reactions are (i) CO adsorption on the surface, (ii) O₂ dissociation into O adatoms on surfaces, and (iii) CO + O \(\rightarrow\) CO₂ reaction on the surface. Accordingly, the reaction rate depends on the favourable activation of both adsorbed CO and O₂. This occurs by the transfer of electrons from the Fermi level of CoFeZnNiGa alloy surface to the lowest unoccupied molecular orbital (LUMO) of CO or O₂, which are antibonding in nature for the both [33, 34].
Figure 3: Comparison of Fermi level energy of CoFeZnNiGa alloy with energy of LUMO of (a) O₂ and (b) CO, (c) Interaction of Π* orbital of O₂ with the pₓ and (d) dₓz orbital of metals on the surface.

To understand the factors contributing to the initial adsorption of reactant molecules, energies of Fermi level (E_F) of surface of the CoFeZnNiGa alloy and LUMO (E_LUMO) of CO and O₂ were compared (Figure 3(a,b)). E_F of metallic CoFeZnNiGa alloy surface is -4.29 eV, which is energetically lower from E_LUMO (-0.24 eV) of O₂ than E_LUMO (-2.71 eV) of CO. Therefore, electron transfer from the catalytic surface to O₂ is more difficult than to CO. Adsorption of CO on the surface depletes the electron availability for the activation of O₂. Hence, the adsorption and the dissociation of O₂ were considered to be the first step followed by adsorption of CO. To
understand the most favourable adsorption sites of O\textsubscript{2} and CO, their orbital interaction with the surface was considered. For both O\textsubscript{2} and CO, the LUMO is $\Pi^*$ orbital and hence more prone to interact with the $p_x$ or $p_y$ orbitals of Ga and $d_{xz}$ or $d_{yz}$ orbitals of Co, Ni, Fe, Zn atoms on the surface Figure 3(c,d). Therefore, a particular atom having more filled states contributed from previously considered orbitals near the Fermi level has more potentiality to transfer the electron for adsorption and activation of O\textsubscript{2} and CO. Being more stabilized on the hollow sites, for the adsorption of O\textsubscript{2}, the average value of the filled states within 1 eV near the Fermi level of different hollow sites on the surface was calculated. A particular hollow site containing only Ni atoms came out to be the most suitable adsorption site according to the criteria; Figure 4(a). Optimized structure of adsorbed O\textsubscript{2} on the chosen hollow site leads to the spontaneous formation of 2O* adsorbed on different sites, indicating high activity of CoFeZnNiGa alloy surface. Hence, the adsorption of only one O* was considered as stability of this particular intermediate determines the feasibility of the first elementary step.

In the next step, a similar exercise was done to find out the most suitable adsorption site for CO on the surface containing O*. A particular hollow site containing only Ni-atoms next to the adsorption sites of O maintained the aforementioned criteria (Figure 4(b). After the adsorption of CO, in the neighbouring O site on the CoFeZnNiGa alloy surface, the structure was optimized. The free energy diagram was calculated to understand the rate-determining step in the considered mechanistic pathway (Figure 5). Adsorption of O on the surface is less endothermic (0.56 eV) as compared to that of (1.13 eV) of adsorption of CO. This is obvious as initially adsorbed O pulls surface electrons, making the stabilization CO difficult. Desorption of CO\textsubscript{2} from the surface is highly exothermic, putting CoFeZnNiGa alloy surface forward as an active catalyst for CO oxidation reaction.
Figure 4: (a) Average value of density of states of the hollow sites on the CoFeZnNiGa alloy surface contributed by \( p_x \) and \( p_y \) orbital for Ga atom and \( d_{xz} \) and \( d_{yz} \) orbital for Co, Fe, Ni, Zn atoms within 1 eV near the fermi level (b) Average value of density of states of the hollow sites on the CoFeZnNiGa alloy surface with adsorbed O* contributed by \( p_x \) and \( p_y \) orbital for Ga atom and \( d_{xz} \) and \( d_{yz} \) orbital for Co, Fe, Ni, Zn atoms within 1 eV near the Fermi level.
Figure 5: (a) Free energy diagram of CO oxidation over CoFeZnNiGa alloy surface, (b) CO and O adsorbed over the CoFeZnNiGa alloy surface. Purple ball represents O and Red call represents the O of CO.

Conclusions

Catalytic CO oxidation over low-cost novel CoFeZnNiGa HEA nanoparticles, synthesized by cast-cum-crush method was carried out in the presence of the feed oxygen. The conversion and selectivity curves of CO oxidation at different GHSV indicate a maximum CO conversion of 99.8% was achieved at 175°C and 10,000 GHSV. Activation energy was found to be 3.8 kJ/mol, which is the lowest among the well-studied catalysts in the literature. Rates of the reaction at temperature 313k, 348k, 373k are found out to be 2.38, 5.26, 6.39 μmol/g/sec, respectively. DFT calculations showed the high activity of Ni hollow sites for CO conversion where the rate-determining step is the adsorption of CO having endothermicity of 1.13 eV at the adjacent site of adsorbed O on (111)-oriented surface of the HEA. This is because the d_{xz} and d_{yz} orbitals of the active Ni-atoms contain many filled states near the Fermi level, which can easily transfer.
Materials and method

The pure metal elements were purchased from the Alfa Aesar with 99.99% purity in chips. The nanocrystalline high entropy alloy was prepared by casting-cum-commination method (CCC); details can be seen in previous studies [25, 27]. All five elements were melted in equiatomic ratio under argon environment by arc melting. After multiple melting, an ingot was obtained with a single-phase high entropy alloy. The ingot was parted into small pieces and cryomilled for 7 hours to obtain the nanocrystalline HEA. The extremely low temperature (<123 K) suppress the oxidation and cold welding and provide the free nanoparticles with a pristine surface [25, 27].

Catalytic activity test

The catalytic activities test of CoFeZnNiGa for CO oxidation reaction was carried out in packed bed reactor. A powdered sample was mixed with catalytically inert silica to improve the flow characteristics of the reactants and the heat distribution in the catalyst. The catalyst bed was loaded with 110 mg of the sample in a tubular quartz tube (25 cm length and 4 mm internal diameter). Both the ends were plugged with the help of quartz wool. This tube was introduced into a tubular furnace where the temperature is controlled by a PID controller. For the CO oxidation reaction, carbon monoxide (10% CO+ 90% N_2) and Oxygen (10% O_2 + 90% N_2) were used as the reactants, and additional UHP N_2 was used as the carrier gas. In an experiment, the reaction mixture was passed continuously through the catalyst bed, and the temperature was increased from RT to 400 °C. The ratio of the reactants (CO/ O_2) was maintained as 2:1 and the reactions were performed by varying the space velocity from 10,000 to 40,000 h^{-1}. The feed gas flow rates of O_2 (7sccm) & CO (14sccm) were 21ml/min. (10,000 GHSV), which were controlled by mass flow controllers (ALICAT MC Series). A K-type thermocouple was used to measure the catalyst bed temperature. The outlet gas from the reactor was analyzed by a gas
chromatograph (CIC Baroda) using both a Flame Ionization Detector (FID) and a Thermal Conductivity Detector (TCD). The columns used in the GC were PORAPAK-N and PORAPAK-Q. All the experiments were carried out at atmospheric pressure. The amount of the catalyst used was 110 mg (55mg catalyst+55mg silica).

% Conversion (X) of CO was calculated using the following equations [35] :

\[ X(\text{CO}) = \left( \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \right) \times 100 \]

First, CO was allowed to adsorb on samples at a flow rate of 15ml/min for 30 min at room temperature. The catalyst was then flushed with nitrogen for 30 min at room temperature to remove the gas phase and weakly adsorbed CO. Finally, the catalyst was heated from 25 °C to 400 °C at a constant heating rate of 10°C/min in the presence of nitrogen and desorbed CO and CO₂ was monitored. For the quantification of Conversion of CO, O₂ and the reaction product, calibration of GC was done. A calibration experiment was performed in which the standard gas mixture (CO, CO₂, H₂, N₂) was used. 1 ml of this calibration standard gas was injected in GC, and the areas of different peaks of the gases were noted for the known concentration of the gases. These values were used to find out the moles of each gas in CO oxidation reaction.

**Simulation methodology**

Density functional theory (DFT) were done with “Vienna ab initio simulations (VASP)” package [36]. The Electron-ion interactions were described using all-electron projector augmented wave pseudopotentials, and “Perdew-Bruke-Ernzehof (PBE)” “generalized gradient approximation (GGA)” was used to approximate the electronic exchange and correlations[37]. The plane-wave kinetic energy cut off of 520 eV was used. All the structures were optimized using a conjugate gradient scheme until the energies, and the components of forces reached 10-5 eV and 0.01 eV
Å-1. A vacuum of 10 Å was added in the z-direction to prevent interactions between the periodic images. The Brillouin zone were sampled with 2*4*1 Monkhorst-Pack. DOS calculations for surfaces were performed by sampling the Brillouin zone with 4×8×1 Monkhorst-Pack. Fermi level of CoFeZnNiGa was calculated with respect the local potential. All the calculations were spin-polarized.

Competing interests:

The authors declare no competing interests.

Notes

The authors declare no competing financial interest.

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