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Research paper

Electrochemical and thermal catalytic studies of Co based molybdenum oxide nanomaterials for C—H bond activation

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ABSTRACT

Electrocatalytic and thermal catalytic oxidation of toluene has been investigated by designing a series of $Co_{2-x}Mo_xO_3$ (NA1-NA6). Synthesized nanomaterials were characterized by Powder X-Ray Diffraction, Scanning Electron Microscopy, and Energy-dispersive X-Ray Spectroscopy. Thermal catalytic oxidation of toluene at 150 °C characterized by Gas Chromatography-Mass Spectrometry. Specifically, 19% benzene, 11% benzyl alcohol, and 6% benzoic acid were detected by GC–MS analysis of thermal catalytic oxidation of toluene by NA3. Electrocatalytic activity of the nanomaterials to oxidize water and toluene was studied by Cyclic Voltammetry and Linear Sweep Voltammetry. The peak currents during anodic and cathodic scan depicted that the synthesized materials were actively redox in nature. The onset potential for the electrocatalytic oxidation of toluene in NA3 and NA4 was observed. Samples from electrocatalytic activity were analyzed by High-Performance Liquid Chromatography which gives efficient oxidation of toluene into respective products.

1. Introduction

Activation of the C—H bond has been receiving increasing attention in the last few years [1]. A lot of research is going on the selective modification/transformation of otherwise inert C—H bonds [2–4]. The past two decades have witnessed substantial advancements in transformative tools for C—H bond activation and transformation, predominantly, oxidative C—H/C—H bond transformations have been investigated much [5]. Alkyl aromatic compounds such as toluene constitute an important family of compounds and oxidation of toluene to respective products is a reaction of importance in this context [6–9].

New catalytic pathways have been explored for toluene oxidation in the past few decades which include homogeneous catalysts employing transition metal complexes [10,11]. However, these homogeneous pathways are inefficient for practical or industrial applications due to their high cost, poor selectivity, tedious separation process, and comparatively less scope of recyclability. Researchers have been engaged to overcome these drawbacks by developing some suitable heterogeneous pathways for toluene oxidation. Heterogeneous catalysis [12] getting attention due to easy catalyst separation/recovery, and high recyclability which leads to better catalytic efficiencies and selectivities during oxidation processes [13]. As Raja and coworkers [14] designed single-site heterogeneous catalysts for toluene oxidation employing aluminophosphates. Hutchings and co-workers [15] have recently reported an outstanding method for toluene oxidation by molecular oxygen employing Au-Pd alloy nanoparticles as catalysts.

A combination of heterogeneous metal-catalyzed C—H activation with electrocatalysis [16] has been employed for the oxidation of alkyl aromatic compounds owing to the transformation of C—H bonds [17]. The metal-based oxides are being explored immensely now a days for electro-catalyzed C—H activation and transformations owing to their enhanced selectivities and catalytic stabilities [18]. The minimum redox potential required for the desired oxidative purpose has made electrocatalysis an ideal platform for the oxidative C—H transformations in

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Received 30 September 2020; Received in revised form 14 December 2020; Accepted 17 December 2020 Available online 25 December 2020 0020-1693/© 2020 Elsevier B.V. All rights reserved. alkyl aromatic compounds [19–23]. These compounds are transformed by reactions with hydroxyl radicals formed from water discharge at the electrode surface under anodic polarization [24]. The reactions taking place on the surface of electrodes are oxygen transfer reactions (OTR) [25]. In the first step, oxidation of water on the surface of the catalyst site occurs followed by electrocatalytic oxidation of hydroxyl radical to oxygen or either assistance to oxidation of toluene [26].

Metal oxide-based catalysts are enormously explored for thermal toluene oxidation as they decompose at relatively lower temperatures to give oxygen [27–30]. Also, surfaces of metal oxides contain reactive species such as peroxy/hydroperoxy radicals which have the potential to initiate radical chain reactions and to activate C—H bonds [31–33]. Oxidative C—H activations have been investigated by noble and rare earth metal-based catalysts [34]. Due to their high costs, abundant elements-based metal oxides are getting immense attention for being employed as heterogeneous catalysts in recent times due to their cost effectiveness, non-toxicity, and good thermal stability. Electrochemical water oxidation with Co-based catalysts has been reported [35]. Cobalt nickel molybdenum oxide components for overall water-splitting at high current densities were investigated by Bowen and coworkers [36].

In the light of importance of subject, we have synthesized a series of Co_{2-x}Mo_xO₃ (NA1-NA6) for the purpose of toluene oxidation (via C—H bond activation). The combination of Co and Mo in a single building block could give rise to functional activity for C—H bond activation. Cobalt molybdenum oxide-derived high-performance electrocatalyst have been reported for hydrogen evolution reaction through water splitting [37]. Whereas, Co based molybdenum oxides are explored as modified electrodes for first time for electrocatalytic oxidation of toluene via direct C—H activation in the present work. To check out activity of our modified electrodes exclusively for oxidation of C—H bond of toluene, we have made a comparative investigation of electrocatalytic toluene oxidation with electrocatalytic water oxidation and products of oxidation analyzed by High Performance Liquid Chromatography (HPLC).

2. Materials and methods

2.1. Chemical and reagents

Cobalt acetate, Molybdenum trioxide, Sodium dodecyl sulfate (SDS), Liq·NH3 solution, isooctane, 1–4, dioxane were purchased from Sigma Aldrich. All the chemicals were of analytical grade and used without further purification. Stainless Steel, Parr 5521 high-pressure compact Autoclave used for temperature and pressure treatment.

2.2. Characterization techniques

Powder X-ray Diffraction (PXRD) measurements were performed in an X-ray diffractometer (Bruker, AXS D8) with Cu-Ka radiation (1.5406 Å) at a scanning rate of 10° min in the 2θ range from 10° to 80° . Morphological features of catalysts were characterized by Scanning Electron Microscope (SEM) (JEOL, JSM-6360 EO), and elemental composition was estimated by Energy Dispersive X-Ray (EDX) Spectrometer (JEOL JSM-6360 LV) by taking average of 5 measurements. Catalytic activity monitoring was done by Gas Chromatography-Mass Spectrometry (GCMS) (Shimadzu QP2010, MS Detector SPD 20A). The electrochemical study of the synthesized materials was carried out through cyclic voltammetry, linear sweep voltammetry, and controlled potential coulometry scan. Electrocatalytic activity monitoring was done through High-Performance Liquid Chromatography (HPLC) (Shimadzu, CBM-20A, UV–Vis. Detector SPD 20A, column: C-18 (250 \times 4.6 mm), pump: LC 20AT, Mobile Phase: Acetonitrile, $\lambda = 295$ nm, injection volume: 1.5 µL and temperature: 35 °C).

2.3. Synthesis of Cobalt Molybdenum Oxide Nanomaterials

2.3.1. Synthesis of Co_{1.82}Mo_{0.18}O₃ (NA1)

To synthesize **NA1**, 8.2 g of cobalt acetate was dissolved in 60 ml of water. 1 g of SDS was added to cobalt acetate solution and the mixture was heated slightly under constant stirring. The solution of 0.21 g molybdenum trioxide in 35 ml of liquid ammonia was made separately. Both solutions were added into the tightly closed autoclave reactor, and temperature treatment was given for 5hrs at 140 °C. After completion of reaction mixture was filtered. Precipitates were washed, dried at 80 °C and were grounded to a fine powder. The material **NA1** was obtained as a brown powder that was characterized and utilized for catalytic studies. Powder XRD; Peaks at 20 (6.80, 14.2, 17.62, 21.14, 23.89, 35.08, 44.48, 60.1), Crystallite size (D; 26.09 \pm 3).

2.3.2. Synthesis of Co_{1.54}Mo_{0.46}O₃ (NA2)

Sample NA2 was prepared following the same method as used for NA1. Except for the solution of 0.43 g molybdenum trioxide in 35 ml of liquid ammonia solution was made. The material NA2 was obtained as a brown powder that was characterized and utilized for catalytic studies. Powder XRD; Peaks at 20 (7.90, 17.56, 18.64, 20.88, 22.1, 33.18, 44.44, 60), Crystallite size (D; 20.31 \pm 6).

2.3.3. Synthesis of Co_{1.82}Mo_{0.18}O₃ (NA3)

Sample NA3 was prepared following the same method as used for NA1. Except, 2 ml of isooctane was added to the reaction mixture before adding it into the autoclave. The material NA3 was obtained as a brown powder that was characterized and utilized for catalytic studies. Powder XRD; Peaks at 2 θ (6.70, 20.62, 33.60, 44.50, 60), Crystallite size (D; 27.42 \pm 5).

2.3.4. Synthesis of Co_{1.54}Mo_{0.46}O₃ (NA4)

Sample NA4 was prepared following the same method as used for NA2. Except, 2 ml of isooctane was added to the reaction mixture before adding it into the autoclave. The material NA4 was obtained as a brown powder that was characterized and utilized for catalytic studies. Powder XRD; Peaks at 20 (20.58, 60), Crystallite size (D; 29.23 ± 7).

2.3.5. Synthesis of Co_{1.82}Mo_{0.18}O₃ (NA5)

Sample NA5 was prepared following the same method as used for NA1. Except, 2 ml of 1,4-dioxane was added to the reaction mixture before adding it into the autoclave. The material NA5 was obtained as a brown powder that was characterized and utilized for catalytic studies. Powder XRD; Peaks at 20 (6.80, 20.74, 34.48, 44.60, 60.1), Crystallite size (D; 30.28 ± 9).

2.3.6. Synthesis of Co_{1.54}Mo_{0.46}O₃ (NA6)

Sample NA6 was prepared following the same method as used for NA2. Except, 1,4-dioxane was added to the reaction mixture before adding it into the autoclave. The material NA6 was obtained as a brown powder that was characterized and utilized for catalytic studies. Powder XRD; Peaks at 20 (20.82, 33.88, 44.30, 60), Crystallite size (D; 32.51 \pm 7).

2.4. Thermal Catalytic Study

The catalytic activity of synthesized nanomaterials was studied by carrying out the thermal catalytic oxidation of toluene in Teflon lined autoclave container. For the study, 0.05 g of each synthesized material **(NA1-NA6)** and 10 ml of toluene was added to the autoclave container. The autoclave was closed tightly and kept in the furnace for 1 h at 150 °C. After that sample was filtered out and characterized by GC–MS analysis.

EDX Parameters for Synthesized Nanomaterials (NA1-NA6).

Samples	Expected Unit Formula	Found Unit Formula	Found Percentage Composition	Color/ Nature
NA1	Co _{1.82} Mo _{0.18} O ₃	Co _{1.82} Mo _{0.18} O ₃	Co(62.17); Mo (10.01); O (27.82)	Brown Powder
NA2	Co _{1.54} Mo _{0.46} O ₃	$Co_{1.54}Mo_{0.46}O_3$	Co(49.62); Mo (24.13); O (26.24)	Brown Powder
NA3	Co _{1.82} Mo _{0.18} O ₃	Co _{1.82} Mo _{0.18} O ₃	Co(62.17); Mo (10.01); O (27.82)	Brown Powder
NA4	Co _{1.54} Mo _{0.46} O ₃	Co _{1.54} Mo _{0.46} O ₃	Co(49.62); Mo (24.13); O (26.24)	Brown Powder
NA5	Co _{1.82} Mo _{0.18} O ₃	Co _{1.82} Mo _{0.18} O ₃	Co(62.17); Mo (10.01); O (27.82)	Brown Powder
NA6	Co _{1.54} Mo _{0.46} O ₃	$Co_{1.54}Mo_{0.46}O_3$	Co(49.62); Mo (24.13); O (26.24)	Brown Powder

2.5. Electrocatalytic Study

An electrocatalytic study was done by literature reported methods with some modifications [35,36,38]. An electrochemical cell was established by using modified glassy carbon as a working electrode, Ag/ AgCl electrode as a reference electrode, and platinum wire as a counter electrode. All these electrodes were dipped in electrolytic solutions. Two different electrolytes i.e. 0.001 M KOH and NaOH were used. These electrolytic solutions were standardized before they were used against KHP. Synthesized nanomaterials **NA3** and **NA4** were employed as a modified working electrode. To modify the working electrode, the very dilute slurry was prepared by grinding the synthesized material in ethanol using PVP as a binder. A very minute drop of the slurry was applied on the glassy carbon electrode which was dried and connected to the potentiostat device. The electrolyte media was subjected to slow stirring during the electrochemical experiment.

Electrocatalytic water oxidation was studied by employing aqueous solutions of NaOH and KOH whereas electrocatalytic toluene oxidation was carried out by adding the 0.15 ml of toluene in the electrolyte solution using working electrodes modified with **NA3** and **NA4** nanomaterials. Cyclic voltammetric (CV) and linear sweep voltammetric (LSV) experiments were carried out by varying the scan rates i.e. 5, 10, 20, 40, 60, 80, 100 mV/s in 0.001 M KOH and NaOH.

3. Results and discussion

3.1. Characterization of Nanomaterials (NA1-NA6)

3.1.1. Elemental Analysis by EDX

The elemental analysis of all the samples was carried out by Energy Dispersive X-ray (EDX) analysis technique coupled with Scanning Electron Microscopy (SEM). The EDX images obtained in this case are presented in Fig. S1 (supplemental data). The expected elemental composition and found percentages of individual elements in this respect are reported in Table 1.

EDX image of **NA1-NA6** exhibited various peaks for cobalt molybdenum and oxygen with a varying intensity which confirmed the presence of all these elements in samples. The high-intensity peak of cobalt was observed in the range of 2.2 to 2.4 keV and 6.8 to 7 keV for the synthesized nanomaterials. Whereas molybdenum also exhibited highintensity peaks at 0.3, 7.6, and 9.8 keV for all the samples. Co was present as a major elemental composition for all the synthesized nanomaterials and Mo was present as minor elemental composition as enlisted in Table 1.



Fig. 1. PXRD Pattern of Nanomaterials **(NA1-NA6)**. [Diffraction Peaks of Co_2O_3 agree well with Standard Pattern (JCPDS:9–418) while Diffraction Peaks of MoO_2 corresponds with Standard Pattern (JCPDS:71–1423) and diffraction peaks of $CoMoO_4$ were in accordance to (JCPDS: 21–0868)].

3.1.2. Powder X-Ray Diffraction (PXRD) Analysis

PXRD patterns of nanomaterials **(NA1-NA6)** are presented in Fig. 1. Powder patterns of synthesized nanomaterials were matched with standard powder patterns. Specific hkl values (311), (222), (511), (101), and (002) were evaluated corresponding to 2theta values. These values were matched with standard PXRD patterns of Co_2O_3 (JCPDS:9–418) [39], MoO₂ (JCPDS:71-1423) [40] and CoMoO₄ (JCPDS: 21-0868) [41]. All the diffraction peaks of samples indexed to the hexagonal structure having *P63mc* space group [40] in accordance with the standard data of Co_2O_3 (JCPDS:9–418). The peaks marked '•' were attributed to Co_2O_3 (JCPDS:9–418). This trend suggested Co_2O_3 as a major phase of synthesized materials **(NA1-NA5)** whereas minor phase represented by MoO₂ (JCPDS:71-1423).

Samples **(NA1-NA5)** have shown peak intensities at 20 (14.2, 35.08, 44.48, 60.1) corresponds to major phase Co_2O_3 corresponds to the (311), (222), (511) hkl lattice planes of the hexagonal structure whereas peak intensities at 21.14, 23.89, and 6.80, 17.62 represented by minor phases of MoO₂ and CoMoO₄ respectively. These peak assignments in PXRD indicated that sample **NA1-NA6** are composite materials having crystalline phases Co_2O_3 , MoO₂, and CoMoO₄ in it.

After PXRD phase assignments, other parameters i.e. crystallite size, dislocation densities, crystallite volume, and microstrain were calculated for all the synthesized materials and reported in Table 2. Particle size calculation is performed using the Debye Sherrer formula [42] as follows:

$$D = 0.91\lambda/\beta cos\theta \tag{1}$$

where D is the particle size of the sample and λ is the wavelength of the X-ray diffraction beam and has a value of 1.54Å. The angle at which diffraction occurs is cos θ , and β is the FWHM (full width at half maximum) value [43].

The volume of crystalline (V) is calculated using the relation ($V = D^3$) [44]. Dislocation density (δ), which represents the extent of defects in the sample is defined as the length of dislocation lines per unit volume of the crystal and is calculated using Eq. (2) [45].

$$\delta = 1/D^2 \tag{2}$$

The strain-induced broadening in powders due to crystal imperfection and distortion is calculated as microstrain (ε) [46]. Positive values of ε represent tensile strain while a negative value represents compressive strain [47]. Micro strain for nanomaterials was calculated by Eq. (3) [46] as follows:

Synthetic Conditions, Composition, and PXRD Parameters of Synthesized Nanomaterials (NA1-NA6).

Samples	Synthetic Conditions	FoundComposition (From EDX)	Average Crystallite SizeD (nm)	$\begin{array}{l} VolumeV = \\ D^3 \end{array}$	Dislocation Density \times 10 ⁻³ (δ) (nm) ⁻²	Micro Strain(ε)
NA1	8.2 g of Co(OAc) ₂ ·4H ₂ O, 0.21 g MoO ₃ , 35 ml Liq·NH ₃ ,1 g SDS	Co _{1.82} Mo _{0.18} O ₃	$\textbf{26.09} \pm \textbf{3}$	17,759	$1.48 imes 10^{-6}$	0.039
NA2	8.2 g of Co(OAc) ₂ .4H ₂ O, 0.43 g of MoO ₃ , 35 ml of Liq·NH ₃ , 1 g of SDS	$Co_{1.54}Mo_{0.46}O_3$	20.31 ± 6	8378	$2.5 imes 10^{-6}$	0.049
NA3	8.2 g of Co(OAc) ₂ .4H ₂ O 0.21 g MoO ₃ , 35 ml liq·NH ₃ , 1 g SDS, 2 ml isooctane	$Co_{1.82}Mo_{0.18}O_3$	$\textbf{27.42} \pm \textbf{5}$	20,615	$1.37 imes10^{-6}$	0.037
NA4	8.2 g of Co(OAc) ₂ ·4H ₂ O,0.43 g of MoO ₃ , 35 ml Liq·NH ₃ , 1 g SDS, 2 ml isooctane	$Co_{1.54}Mo_{0.46}O_3$	29.23 ± 7	24,973	$1.19 imes10^{-6}$	0.035
NA5	8.2 g of Co(OAc) ₂ .4H ₂ O, 0.21 g MoO ₃ , 35 ml Liq·NH ₃ , 1 g SDS, 2 ml 1,4-dioxane	$Co_{1.82}Mo_{0.18}O_3$	30.28 ± 9	27,763	$1.11 imes10^{-6}$	0.034
NA6	8.2 g of Co(OAc) ₂ .4H ₂ 0, 0.43 g of MoO _{3,} 35 ml liq·NH ₃ , 1 g SDS, 2 ml 1,4-dioxane	$Co_{1.54}Mo_{0.46}O_3$	32.51 ± 7	34,359	$9.47 imes 10^{-7}$	0.032



Fig. 2. SEM Images of (NA1-NA6) at 1 µm Resolution; [(a) NA1 (b) NA2 (c) NA3 (d) NA4 (e) NA5 (f) NA6].

(3)

$\varepsilon = \beta/4tan\theta$

Average crystallite sizes for nanomaterials (NA1-NA6) at their corresponding intensities for each phase were calculated separately. For the major phase, Co_2O_3 crystallite sizes were found to be in the range of 23–30 nm whereas for the minor phases MoO_2 and $CoMoO_4$ crystallite sizes were found to be in the range of 19–22 and 22–29 nm respectively. Average crystallite sizes of the synthesized materials including all the representing phases were 26.09 \pm 3 for NA1, 20.31 \pm 6 for NA2, 27.42 \pm 5 for NA3, 29.23 \pm 7 for NA4, 30.28 \pm 9 for NA5, and 32.51 \pm 7 for

NA6. It was noted that the crystallite size was increased by the increment in the ratio of molybdenum which causes the crystal stress due to which minute shifts in some peaks were observed. Values of dislocation density show the extent of defect found to be less in nanomaterials having smaller crystallite size showing greater stability. Volume indicates that there is proper incorporation of cobalt and molybdenum ions into regular lattice sites of O- in the samples. Positive values depicted tensile microstrain in synthesized nanomaterials which can be due to the lattice shrinkage observed in the calculation of lattice

Morphological Characteristics of Synthesized Nanomaterials (NA1-NA6) by SEM Analysis.

Samples	Material Nature	Dispersity	Structural Appearance
NA1	Composite	Heterogeneous	Broad Elliptical, Irregular
NA2	Composite	Heterogeneous	Broad Elliptical, Irregular
NA3	Composite	Heterogeneous	Broad Elliptical, Rugged Surface
NA4	Composite	Heterogeneous	Broad Elliptical, Irregular
NA5	Composite	Heterogeneous	Agglomerated Rugged Surface
NA6	Composite	Heterogeneous	Broad Elliptical, Irregular



Fig. 3. Gas Spectrum (GC) Toluene Oxidation Product (T-NA3) after Catalytic Thermal Oxidation Activity.

GC–MS Data of Toluene Oxidation Product (T-NA3) after Catalytic Thermal Oxidation Activity.

GC Peak No.	Retention Time(RT)	m/z of MolecularIon Peak	Name	Concentration (%)
1	6.1	79	Benzene	19
2	6.7	99	Cyclohexanol	08
3	7.7	111	Benzyl alcohol	11
4	8.1	113	1,2- dihydroxybenzoic acid	05
5	12.6	123	Benzoic acid	06

parameters causing the crystal stress due to which little shift in some peaks was observed [48].

3.1.3. Scanning Electron Microscopy (SEM) Analysis

SEM micrographs of nanomaterials (NA1-NA6) are shown in Fig. 2 (a)-(f) and morphological characteristics are enlisted in Table 3. NA1 showed heterogeneous morphology incorporating some broad elliptical structures with irregular patterns. SEM micrographs of NA2 exhibited irregular morphology incorporating some elliptical leaf-like structure. SEM micrographs of NA3 and NA4 showed non-uniform morphology showing some agglomerated structures with rugged appearance. SEM micrographs showed heterogenized morphology incorporating some agglomerated rugged structures for NA5 and broad elliptical irregular surface for NA6. Compounds were found to be composite from surface morphological features which are in accordance with PXRD results.

3.2. Catalytic Thermal Oxidation of Toluene

3.2.1. GCMS Analysis of Toluene Oxidation Products

GCMS Analysis of the liquid product of toluene oxidation (**T-NA3**) was carried out. The gas chromatogram is shown in Fig. 3. which is characterized by different peaks representing the functionalities produced after oxidation of toluene (enlisted in Table 4). MS corresponds to high-intensity GC signals are given in section S2 (supplemental data) with the structure of the expected compound present. Peak 1 (RT = 6.1) represents 19% benzene (m/z = 79) which is basic structure in toluene. Peak 2 (RT = 6.7) attributed to 08% of cyclohexanol (m/z = 99) and Peak 3 (RT = 7.7) corresponds to 11% benzyl alcohol (m/z = 111) which is basically the oxidation product of toluene [8]. Peak 4 (RT = 8.1) is due to 05% of 1,2-dihydroxybenzoic acid (m/z = 113) and Peak 5 (RT = 12.6) representing 06% of benzoic acid (m/z = 123) formed during the toluene oxidation process [49].

3.3. Electrocatalytic Oxidation Study

Cyclic voltammetry (CV) studies of sample **NA3** was carried out to study electrocatalytic water oxidation in an aqueous solution of KOH (0.001 M) and NaOH (0.001 M). The sample was scanned between 0.2 and 0.9 V at various scan rates i.e. 5, 10, 20, 40, 60, 80, 100 mV/s to check out the catalytic stability of the material. Samples after electrocatalytic activity were analyzed by HPLC analysis. Higher catalytic current values were observed at higher scan rates.

The cyclic voltammogram of **NA3** in NaOH is shown in Fig. 4. At a moderate scan rate of 100 mV/s, voltammogram observed a broad feature in the anodic scan at 0.58 V, followed by a sharp onset of catalytic anodic current with a value of 6.45μ A. During a reverse cycle, the sluggish cathodic peak was observed at 0.6 V generating current with



Fig. 4. Cyclic Voltammogram of NA3 in aq. NaOH (A) and after the addition of Toluene (B) Scanned Between 0.2 and 1.2



Fig. 5. Cyclic Voltammogram of NA3 in aq. KOH (A) and after the addition of Toluene (B) Scanned Between 0.2 and 1.2



Fig. 6. Linear Sweep Voltammograms of NA3 in 0.001 M KOH and 0.001 M NaOH Scanned at 20 mV/s



Fig. 7. Cyclic Voltammogram of NA4 in aq. NaOH (A) and after the addition of Toluene (B) Scanned Between 0.2 and 1.2

negative values $-5.8 \ \mu$ A. Anodic and cathodic signals represented the active redox behavior of the **NA3** catalyst. In Fig. 4, peaks are very clear and there is no change in the peaks while moving from lower to the higher scan rate which exhibits the stability of the catalyst.

The cyclic voltammogram of **NA3** in KOH is depicted in Fig. 5. In the absence of toluene, a voltammogram showed the oxidation and reduction of **NA3**. But in the presence of toluene, the cathodic peak current increases significantly at 0.6 V, while the corresponding anodic peak appeared at the same potential values exhibiting the oxidation process.

Linear sweep voltammetry was also carried out to check the onset potential for catalytic oxidation of water and toluene. The corresponding LSVs of the OER at **NA3** modified GC electrodes were recorded in 0.001 M KOH and 0.001 M NaOH at 20 mV/s scan rate (Fig. 6). LSV was performed with water and in the presence of toluene in the electrolytes NaOH and KOH. The onset potential for the electrocatalytic oxidation appeared to be at 1.25 V at 20 mV/s scan rate. After this potential value, the constant increase in catalytic current was observed parallel to the potential.

Cyclic voltammetry study of sample **NA4** was also carried out scanning between -0.8 to1.2 V for examining electrocatalytic water oxidation in an aqueous solution of 0.001 M NaOH employing different scan rates i.e. 5, 10, 20, 40, 60, 80, 100 mV/s. A quasi-reversible electron transfer was observed in presence of aq. NaOH as shown in Fig. 7(A) and (B). Two prominent redox couples were observed. Higher catalytic current values were observed at higher scan rates. At a scan rate of 100 mV/s, a voltammogram revealed two anodic peaks at 0.03 V and 0.7 V,



Fig. 8. Cyclic Voltammogram of NA4 in aq. KOH (A) and after the addition of Toluene (B) Scanned Between 0.2 and 1.2



Fig. 9. Linear Sweep Voltammograms of NA4 in 0.001 M KOH and 0.001 M NaOH Scanned at 20 mV/s



Fig. 10. HPLC of Toluene and its Oxidation Products (T-NA3) after electrocatalytic study in KOH and NaOH

followed by the onset of catalytic anodic current with a value of 1.7 μ A and 38.4 μ A respectively. During a reverse cycle, two sharp cathodic peaks were observed at 0.5 V and -0.3 V generating current with negative values, -21.5 and -33 μ A respectively.

The cyclic voltammogram of **NA4** in KOH is depicted in Fig. 8. In the presence of toluene, two anodic peaks and two cathodic peaks representing oxidation and reduction of the toluene were observed at various scan rates. The values of the catalytic current increased with an increase

in the scan rate. In the absence of toluene, a voltammogram showed the oxidation and reduction of **NA3**. But in the presence of toluene, the cathodic peak current increases significantly at 0.6 V, while the corresponding anodic peak appeared at the same potential values exhibiting the oxidation process.

Linear sweep voltammetry confirmed the onset potential for catalytic oxidation of water and toluene in 0.001 M KOH and 0.001 M NaOH as shown in Fig. 9. The corresponding LSVs of the OER at **NA4** modified GC electrodes were recorded in 0.001 M NaOH at a scan rate of 20 mV/s. LSV was performed before the addition of toluene, and after the addition of toluene. The onset potential for the electrocatalytic oxidation appeared to be at 1.27 V at both the scan rates. After this potential value, the constant increase in catalytic current was observed parallel to the potential.

Overall results of electrochemical studies indicated efficiency of our catalysts as modified electrodes for toluene transformation into oxidation products. These oxidation products are further analyzed by HPLC.

3.4. Analysis of Electrocatalytic Toluene Oxidation Products

3.4.1. HPLC analysis

Toluene has a single peak in HPLC chromatogram at 3.9 retention time as shown in Fig. 10 which indicated the affinity of the toluene with the stationary phase. Polar acetonitrile was used as a mobile phase. Elution time characterized the sample to be of higher molecular weight and high-intensity peak indicating a high toluene concentration which is expected to decrease after the oxidation activity. Different parameters from HPLC of toluene are enlisted in Table 5. Response factor [50] was calculated for known toluene concentration injected as follows:

Response Factor (RF) = Peak Area/Concentration of Toluene (4)

HPLC Data of Toluene and its Oxidation Products (T-NA3) after Electrocatalytic Study in KOH and NaOH.

Peak No.	HPLC Data of Toluene Oxidation Products					
	Retention Time (min)	Intensity	Peak Area	Response Factor (RF)	Concentration(mg/mL)	
Toluene						
T1	3.9	100.3	1,852,360	3704.72	500	
T-NA3 (NaOH)						
1	1.9	100.12	34,135	68.18	9.22	
2	2.26	39.99	42,884	85.68	11.58	
3	2.73	13.52	11,431	22.78	3.09	
4	3.2	10.93	8962	17.83	2.42	
5	4.26	14.75	4151	8.21	1.12	
T-NA3 (KOH)						
1'	1.60	7.35	6413	12.74	1.73	
2'	1.96	100	24,388	48.69	6.58	
3'	2.38	9.80	12,754	25.42	3.44	
4′	2.60	65.9	17,607	35.12	4.75	
5′	3.03	14.65	9306	18.52	2.51	

Electrocatalytic efficiency of synthesized nanomaterials was monitored by HPLC after the electrochemical oxidation of toluene into its respective products. Different parameters of toluene oxidation products (**T-NA3**) after electrocatalytic study in KOH and NaOH electrolytes are enlisted in Table 5. Concentrations of oxidation products [51] calculated after finding RF from Eq. (4) as follows:

Concentration of oxidation products = Peak Area/Response Factor (5)

Oxidation products of toluene by **NA3** i.e. **T-NA3** (NaOH) and **T-NA3** (KOH) characterized by different peaks in the HPLC chromatogram which exhibits the efficient conversion of toluene into smaller segments after catalytic oxidation. The concentration of toluene got decreased after oxidation activity and toluene peak at 3.9 retention time is almost diminished which was further supported by the concentrations of oxidation products (Table 5).

4. Conclusions

In the current studies, electrocatalytic and thermal catalytic oxidation of toluene has been investigated by a series of Co_{2-x}Mo_xO₃ (NA1-NA6) synthesized by hydrothermal and co-precipitation methods. Synthesized nanomaterials were successfully characterized by PXRD, SEM, and EDX for the elucidation of phase purity and structural composition, and surface morphological characteristics. Thermal catalytic oxidation of toluene was carried out at 150 °C and samples were characterized by GC-MS analysis. 19% benzene, 11% benzyl alcohol, 8%cyclohexanol, and 6% benzoic acid were detected by GC-MS analysis of thermal catalytic oxidation of toluene by NA3. Electrocatalytic activity of the nanomaterials to oxidize water and toluene was studied by Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) employing 0.001 M KOH and NaOH as electrolytes. The peak currents during anodic and cathodic scan depicted that the synthesized materials were actively redox in nature. The onset potential for the electrocatalytic oxidation of toluene in NA3 was observed at 1.25 V in KOH and 1.3 V in NaOH whereas onset potential for NA4 appeared at 1.22 V in KOH and 1.27 V in NaOH. Samples from electrocatalytic activity were analyzed by High-Performance Liquid Chromatography (HPLC) which gives efficient oxidation of toluene into respective products characterized by different peaks in HPLC of oxidation products.

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CRediT authorship contribution statement

Samia Kausar: Conceptualization, Methodology, Investigation. Noor ul Ain: Methodology, Investigation. Ataf Ali Altaf: Writing - review & editing, Project administration, Funding acquisition, Supervision. Muhammad Danish: Resources. Anmol Basit: Methodology, Investigation. Bhajan Lal: Resources, Formal analysis. Shabbir Muhammad: Resources. Amin Badshah: Resources, Formal analysis. Hafiz Muhammad Kashif Javaid: Resources.

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.

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Appendix A. Supplementary data

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