Enhanced catalytic reduction of para-nitrophenol using α-MoO$_3$ molybdenum oxide nanorods and stacked nanoplates as catalysts prepared from different precursors

Mostafa Abboudia,*, Hicham Oudghiri-Hassania,*, Fahd Al Wadaanib, Souad Rakass, Ali Al Ghamdia and Mouslim Messalia

aChemistry Department, Taibah University, College of Science, Almadinah, Saudi Arabia; bDépartement de Génie Chimique, Faculté des Sciences et Techniques de Tanger, Université Abdelmalek Essadi, Tangier, Morocco; cDépartement Sciences de la nature, Cégep de Drummondville, Drummondville, Québec, Canada

**ABSTRACT**

Molybdenum oxide, α-MoO$_3$, nanorods and stacked nanoplates were prepared from oxalate, citrate and tartrate precursors. These molybdenum oxides showed high efficiencies in the reduction of para-nitrophenol to para-aminophenol in the presence of NaBH$_4$. The prepared precursors were first characterized by thermal gravimetric analysis (TGA) and then thermally decomposed at 350°C (oxalate precursor) and 550°C (citrate and tartrate precursors). The final oxides were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and the Brunauer–Emmet–Teller (BET) technique. The oxalate precursor is the most efficient catalyst for the reduction reaction.

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1. Introduction

In the last few decades, important studies have been performed on transition metal oxides, specifically MoO$_3$, molybdenum oxide. MoO$_3$ can exist in three allotropic forms, α-MoO$_3$ orthorhombic, β-MoO$_3$ monoclinic and γ-MoO$_3$ hexagonal. MoO$_3$ has a wide range of applications as a catalytic, optic, sensor material; solar cell component; or solid oxide fuel cell [1–10]. The layered structure with stacking along the [010] direction presented by α-MoO$_3$ also means that it could be used as a cathode in lithium batteries [11–18]. It is well known that the shape and/or size of particles can greatly influence the chemical and physical properties of materials. Many studies describe methods to obtain MoO$_3$ with different nanostructures. The nanostructures include nanobelts, nanorods, nanoplates, nanotubes, nanoflakes, nanoribbons, nanofibers, nanosheets, nanoplatelets or nanowires that were synthesized as powders or deposited as films using different experimental methods, such as hydrothermal, solvothermal, solvo-combustion, spray pyrolysis, thermal evaporation or electrochemical processes [19–30].

This study presents a new method for the synthesis of α-MoO$_3$ nanomaterials that is solvent free using the thermal decomposition of molybdenum complexes prepared in a solid state. Additionally, the study presents results about the catalytic performance of α-MoO$_3$ materials prepared using this new method in the reduction of the para-nitrophenol to para-aminophenol. The para-nitrophenol is considered an extremely dangerous and harmful chemical. It is toxic and carcinogenic and can cause dangerous impact in aquatic environments. It has been classified as priority pollutant [31]. On the other hand, this nitroaromatic compound is used for the synthesis of the aminophenol an important intermediate to produce pharmaceuticals analgesics like paracetamol or acetaminophen. The para-nitrophenol is found in many industrial effluents such as petrochemicals, petroleum refineries, leather, insecticides and herbicides industries.

2. Experimental

2.1. Synthesis of α-MoO$_3$ catalysts

In this study, molybdenum oxide, α-MoO$_3$, was synthesized using the thermal decomposition of the three precursors of molybdenum obtained from the reaction of ammonium molybdate (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O and a carboxylic acid in the solid state, namely, oxalic acid, H$_2$C$_2$O$_4$.2H$_2$O; citric acid, C$_6$H$_8$O$_7$ and tartaric acid, C$_4$H$_6$O$_6$ [32]. In a typical procedure, ammonium molybdate (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O and carboxylic acid were mixed in a ratio of Mo: acid of 1:3. The mixture
was ground until good homogeneity was observed and then heated on a hot-plate at 160°C for the oxalic acid case and 180°C for the citric acid and tartaric acid cases. Then, the three precursors were decomposed at temperatures deduced from the thermal gravimetric analyses. The oxalic precursor (MoOxal) was decomposed at 350°C and the citric (MoCit) and tartaric (MoTart) precursors were decomposed at 550°C in a tubular furnace open on both ends.

2.2. Characterization

An SDT Q 600 analyzer was used for the thermal analyses of the precursors. To identify the resulting materials and verify their purity, the powder X-ray diffraction technique was conducted using an XRDP-6000-Shimadzu, X-ray diffractometer (40 kV/20 mA) in the conventional θ–2θ reflection geometry using Cu Kα radiation (λ = 1.5406 Å). Scanning electron micrographs of the samples were obtained from a Shimadzu Super-Scan SSX-550. The adsorption–desorption isotherms were recorded using a Micromeritics ASAP 2020 surface area and porosity analyzer. Particle sizes were estimated using the equation $D_{BET} = \frac{6000}{\rho S}$, where $\rho$ is the density (4.711 g/cm³) and S is the specific surface area. A Varian Cary 100 UV–visible spectrophotometer was used to measure the variation of the para-nitrophenol concentration.

2.3. Catalytic activity test

The prepared molybdenum oxide materials were evaluated as catalysts in the reduction reaction of para-nitrophenol, C₆H₄OH(NO₂), with sodium tetrahydroborate, NaBH₄, to para-aminophenol, C₆H₄OH(NH₂). The catalytic tests were conducted as follows: 40 mL of a sodium tetrahydroborate NaBH₄ solution (8 × 10⁻⁴ M) was added under continuous stirring to 40 ml of a para-nitrophenol solution at 4 × 10⁻⁴ M. Then, an intense yellow color appeared because of the formation of a para-nitrophenolate anion in the solution. To the resulting solution, 0.1 g of the molybdenum oxide catalyst was added. The phenolate maximum band absorption was observed at 401 nm, and the reaction evolution was monitored using a UV visible spectrophotometer.

3. Results and discussions

3.1. Characterization of materials

In the first step, the thermal gravimetric analyses were performed for the three precursors. In Figure 1, it is seen that the oxalate precursor MoOxal thermal gravimetric curve is different from the curves of MoCit and MoTart. The last weight loss is observed at 250°C for MoOxal, which differs from the citrate and tartrate precursors that are decomposed until 450°C. Indeed, the precursors were heat treated as stated above at 350°C for MoOxal and 550°C for MoCit and MoTart. Figure 2 depicts the XRD patterns of the samples that crystallize in the orthorhombic symmetry. All of the peaks were indexed in accordance with J.C.P.D.S. file #75-0912, which results in parameters $a=3.920\,Å$, $b=13.94\,Å$ and $c=3.660\,Å$. An important difference is observed in the peak intensity for (020), (040) and (060) reflections located at 2θ values 12.69°, 25.54° and 36.73°, respectively. In the case of the citric and tartaric precursors, the intensity is higher than the case of the oxalic acid precursor. This result confirms that the stacking of the plates along the [010] direction is conducive to the (0k0) preferential orientation. As seen in Figure 3(a), the particles of molybdenum oxide prepared from the oxalate precursor have nanorods shape with a diameter of less than 100 nm. However, in Figure 3(b,c),...
The stacking of plates is observed, which is in good agreement with the XRD results that show a preferential orientation. These particles are classified as nanoplate shapes because their heights are less than 100 nm stacked along [0k0]. Furthermore, measurements of the adsorption–desorption curves in the BET (Braunauer–Emmet–Teller) reveals the nanoscale character for the sample prepared from MoOxal. The specific surface area values are 41.02, 0.35 and 0.34 m²/g for samples prepared from MoOxal, MoCit and MoTart, respectively. The corresponding particle sizes are 31 nm, 3.74 microns and 3.75 microns, which agrees with the SEM observation that shows the difference between the α-MoO₃ samples in shape and size, in which the case of MoOxal has nanorods and MoCit and MoTart have stacked nanoplates. The difference is attributed to the experimental conditions, especially the temperature of the heat treatment for MoOxal at 350°C and 550°C for MoCit and MoTart. As example the adsorption–desorption curves for the sample prepared from MoOxal are given in Figure 4 (a), where type IV is obtained. The closure to P/P₀ to 0.4 indicates the presence of small mesopores. In the left side of the curves rounded knee indicates approximate location of monolayer formation. The low slope region in middle of isotherm indicates first few multilayers formation. The existence of the hysteresis indicates capillary condensation in meso and macropores. In Figure 4(b) the t-plot curve is represented and shows that the intercept with the Y-axis is near zero showing the small micropore volume. On the other hand the pore size distribution and volume size distribution could be estimated using Barrett–Joyner–Halenda (BJH) method and are found to be of 77 Å and 0.0975 cm³/g.

3.2. Catalysis study

In Figure 5, a comparison of the catalytic activity of the prepared samples in the reduction of para-nitrophenol is presented. All of the samples are efficient as catalysts in this reaction. In these graphs, the band intensity at 401 nm decreases, while the band at 317 nm, which indicates the formation of para-aminophenol, increases as time increases. The best results were obtained with the sample prepared using the oxalate precursor MoOxal (Figure 3(a)), in which the reaction is almost instantaneous, with a final reaction time less than 30 s instead of 6 min for samples prepared using MoCit and MoTart. A higher specific surface area and lower crystallites size were the determinant factors in the higher catalytic efficiency of the sample prepared using MoOxal. This is in accordance with several works where it was observed a higher efficiency citing the impact of the particles size when decreasing and the specific surface area increasing [33, 34]. However, no difference in the mechanism can be proposed for all of the catalysts. The reactive entities will be created from the homolytic dissociation of the BH bond in NaBH₄, which results in the formation of reactive species MoO₃−H and MoO₃−BH₄⁻ (Equation (1)) that will reduce the para-nitrophenol (PNP) to the para-aminophenol (PAP) where six electrons are involved (Equations (2) and (3)) [35, 36].

\[ 2\text{MoO}_3 + \text{BH}_4^- \leftrightarrow \text{MoO}_3 - \text{H} + \text{MoO}_3 - \text{BH}_4^- \]  

(1)

\[ 6\text{MoO}_3 - \text{H} + \text{PNP} \rightarrow \text{PAP} + 6\text{MoO}_3 + 6\text{H}^+ \]  

(2)

\[ 6\text{MoO}_3 - \text{BH}_4^- + \text{PNP} \rightarrow \text{PAP} + 6\text{MoO}_3 + 6\text{BH}_3 \]  

(3)
Nanorods of α-MoO₃ molybdenum oxide were successfully prepared by the thermal decomposition of a complex of molybdenum with oxalic acid. For cases of complexes with citric or tartaric acids, micron-sized nanoplates are obtained. The three samples showed high efficiency in the catalytic reduction of para-nitrophenol by NaBH₄. However, in the first case, the molybdenum oxide has a higher specific area (41 m²/g) and is more efficient compared to the two other cases (0.35 and 0.34 m²/g). Note the unusually high efficiency of the sample prepared from the oxalate precursor where the reduction reaction is instantaneous. This example shows that size and shape of crystallite can cause peculiar catalytic properties. In a future study, a more detailed evaluation of the efficiency of this catalyst in the reduction of the nitro function will be presented.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**Figure 4.** N₂ adsorption–desorption isotherms (a), t-plot curve (b), pore area (c) and pore volume distributions (d) of the as-prepared α-MoO₃ catalyst prepared from the MoOxal.

**Figure 5.** Variations of the absorbance versus the wavelength after different reduction reaction times with the α-MoO₃ catalyst prepared using (a) MoOxal heated at 350°C, (b) MoCit heated at 550°C and (c) MoTart heated at 550°C.

**4. Conclusion**

Nanorods of α-MoO₃ molybdenum oxide were successfully prepared by the thermal decomposition of a complex of molybdenum with oxalic acid. For cases of complexes with citric or tartaric acids, micron-sized nanoplates are obtained. The three samples showed high efficiency in the catalytic reduction of para-nitrophenol by NaBH₄. However, in the first case, the molybdenum oxide has a higher specific area (41 m²/g) and is more efficient compared to the two other cases (0.35 and 0.34 m²/g). Note the unusually high efficiency of the sample prepared from the oxalate precursor where the reduction reaction is instantaneous. This example shows that size and shape of crystallite can cause peculiar catalytic properties. In a future study, a more detailed evaluation of the efficiency of this catalyst in the reduction of the nitro function will be presented.
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