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SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF TRANSITION METAL-DOPED MANGANESE OXIDE CATALYSTS R. K. Muya¹, L. Achola², E. C. Njagi^{1*}, O. Ombaka¹, S. L. Suib²

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ABSTRACT: Manganese oxide octahedral molecular sieves exhibit good conductivity, tunable redox properties, high porosity and excellent thermal stability. Thus, these materials have several potential applications as cathodic materials in batteries, adsorbents, catalysts, sensors and electromagnetic materials. In this study, synthetic cryptomelane (K-OMS-2) and framework doped K-OMS-2 materials were synthesized using a facile reflux method. The synthesized materials were characterized using powder X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, Field Emission-Scanning Electron Microscopy (FE-SEM), N₂ sorption, X-ray fluorescence (XRF) and Thermogravimetric analysis (TGA). The synthesized materials were highly crystalline with the structure of tetragonal cryptomelane. Characterization data suggests that dopant cations were incorporated in the structure of K-OMS-2 without the formation of segregated dopant oxides or other impurities. Morphological analyses revealed that K-OMS-2 was composed of nanofibres of ca. 500 nm. The length of the nanofibres decreased significantly on doping K-OMS-2 to form irregular aggregated nanoparticles of ca. 100 nm. Doped K-OMS-2. The V-Cu-Co-K-OMS-2 materials but lower thermal stability than K-OMS-2. The V-Cu-Co-K-OMS-2 material exhibited the highest degradation capacity for methylene blue.

KEYWORDS: Octahedral molecular sieves, manganese oxides, framework doping, methylene blue, degradation.

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1. INTRODUCTION

Industries such as paper, leather, textiles, cosmetic, food, and plastic use dyes to colour their final products [1]. The discharge of these dyes is an environmental health concern more so in developing countries [2]. These dyes should be removed from wastewater before discharging it into water bodies [3]. This is because dyes retard photosynthetic activities since they minimize light penetration in water bodies [1]. In addition, they affect gas dissolution in the water bodies [4]. Methylene blue is one of the most commonly used colouring agents. It has a wide range of applications such as dyeing leather, tannin, printing calico, antiseptic and other medicinal uses [5]. The dye can cause several health problems such as skin and eye irritation, vomiting, nausea, diarrhea, profuse sweating, gastritis and mental confusion [6]. Manganese oxide octahedral molecular sieves (K-OMS-2) are among the materials that can be used to remove dyes from wastewater. Manganese oxides have attracted the interest of many researchers for catalysis, separation, battery materials, energy storage and environmental remediation [7,8] because they are inexpensive, environmentally friendly and are easy to make [9]. The basic structural unit of manganese oxide octahedral molecular sieves is the MnO₆ octahedron [10]. The MnO₆ octahedra are connected through edges and corners to form frameworks with tunnels of diverse sizes [10]. Cryptomelane-type manganese oxide octahedral molecular sieves consist of 2×2 tunnels of 4.6 Å filled with potassium cations [7]. These materials have been investigated for diverse catalytic applications due to their outstanding features such as porosity, ease to release lattice oxygen, presence of acidic sites and redox properties due to mixed valency (2+, 3+ and 4+) of manganese [11]. Introduction of cation(s) either into the K-OMS-2 tunnels or to the framework could be used to tune the structure, morphology, surface area and crystal system which offer novel chemical and physical properties [12]. In the previous studies, K-OMS-2 materials have been doped with one cation, some using low and others high valence ions such as Cu²⁺, Mg²⁺, Ni²⁺, Co²⁺, Zn²⁺, Fe³⁺, V⁵⁺, and W⁶⁺ [13, 14, 15, 16]. Tang *et al.* [17] found that doping K-OMS-2 with vanadium led to enhanced catalytic rates. This was attributed to an increase in surface defect sites for adsorption and excellent surface redox abilities. Sriskandakumar et al. [18] found that doping K-OMS-2 with Mo, V and W led to a significant increase in the activity of the catalyst. In the present study, multiple framework substitution was done on the cryptomelane and the resultant materials were used for the degradation of dyes from synthetic wastewater.

2. MATERIALS AND METHODS

2.1 Chemicals

Chemicals of analytical grade were used without further purification. Sodium metavanadate (NaVO₃; 99.90%), nitric acid (HNO₃; 70%), potassium permanganate (KMnO₄; 99.0%), copper (II) sulphate pentahydrate (CuSO₄.5H₂O; 99.99%), manganese (II) sulphate monohydrate (MnSO₄.H₂O; 99.0%), nickel (II) nitrate hexahydrate (Ni(NO₃)₂ · 6H₂O; 99.99%), iron (II) sulphate heptahydrate (FeSO₄. 7H₂O; 99.0%), cobalt (II) nitrate hexahydrate (Co(NO₃)₂.6H₂O) and methylene blue were

Muya et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications purchased from Sigma-Aldrich. The Merck Milli-Q® IQ 7003/7005 integrated water purification system was used to prepare ultrapure water for synthesis and degradation studies.

2.2 Synthesis

Cryptomelane-type manganese dioxide nanomaterials were synthesized using a reflux method described in the literature [19]. To prepare K-OMS-2, a solution containing 5 g of potassium permanganate in 100 ml of ultrapure water was prepared and labelled solution A. Solution B was prepared by dissolving 7.5 g of manganese sulphate monohydrate in 50 ml of ultra-pure water and subsequently adding 8.5 ml of concentrated nitric acid. Solution B was then added to solution A dropwise with vigorous stirring. The resultant dark brown slurry was refluxed at 100 °C for 24 h, cooled, filtered and washed thoroughly with ultrapure water. The solid sample was then dried at 120 °C for 12 h and powdered to obtain K-OMS-2. To prepare doped K-OMS-2 nanomaterials, requisite amounts of dopant precursors were dissolved in ultrapure water then mixed with solution A and stirred for 2 h to form solution C. Solution B was then added dropwise to solution C with vigorous stirring for ca. 15 min. The resultant dark brown precipitate was refluxed for 24 h at 100 °C, cooled, filtered, washed several times with ultrapure water, dried at 120 °C for 12 h and powdered to obtain doped K-OMS-2 nanomaterials.

2.3 Characterization

Powder XRD diffraction patterns of the synthesized nanomaterials were obtained using a Rigaku Ultima IV diffractometer using Cu K α (λ =0.15406 nm) radiation with a beam of 44 mA and 40 kV. Samples were scanned in the 20 range of 5 ° to 75 ° with a continuous scan rate of 2.0° per minute. The JCPDS database was used to identify the phases. The FT-IR spectra were obtained using a Shimadzu IR Affinity-IS FT-IR spectrophotometer (in the range of 400-4000 cm⁻¹). Manganese dioxide powders were mixed and ground with dry KBr at a ratio of 1:100 and subsequently pressed into transparent pellets. The textural properties of the samples were determined by nitrogen sorption measurements at 77 K using a Quantochrome Autosorb iQ2 analyzer. The specific surface areas of the samples were determined by the Brunauer-Emmett-Teller (BET) method after initial pretreatment of the samples by degassing 150 °C for 12 h. The pore areas and specific pore volumes were determined by the Barrett, Joyner and Halenda (BJH) method after degassing the samples at 150 °C for 1 h and then at 270 °C for 12 h. The morphologies of the samples were determined by field emission scanning electron microscopy (FE-SEM). Samples were prepared for analyses by depositing powders on carbon tapes mounted on stainless-steel holders. Micrographs were then obtained using a Zeiss DSM 982 Gemini field emission scanning electron microscope with a Schottky emitter operating at 2.0 kV with a beam current of 1.0 µA. The thermal stabilities of the samples was studied by thermogravimetric analysis (TGA) using a TA Instruments Q500 Thermogravimetric Analyzer. Samples were loaded onto platinum holders and the temperature raised from ambient to 700 °C at a rate of 10 °C/min under nitrogen gas atmosphere. The elemental

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Muya et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications compositions of the samples were determined by X-ray fluorescence (XRF). Samples were pressed at 20 tons of pressure using an Al ring to form pellets which were then analyzed using a Rigaku ZSX Primus IV XRF spectrometer with rhodium anode X-ray tube generator.

2.4 Degradation of Methylene Blue

The performance of the synthesized materials for degradation of methylene blue was determined using a UV-Vis 1800 Shimadzu spectrophotometer. A 1000 ppm stock solution of methylene blue was prepared by dissolving 1 g of methylene blue in ultrapure water to form 1000 ml solution. The stock solution was then serial diluted to prepare 120, 60, 30 and 20 ppm working solutions. Degradation studies were performed by mixing 50 mg of powdered cryptomelane-type sample with 50 mL of 60 ppm methylene blue solution in a beaker. Aliquots of the resultant mixture were taken at 5 min intervals and filtered using 0.45 μ m PTFE filters. The absorbance of ultrapure water, working standards and the filtrates was recorded at 665 nm. The effects of catalyst loading on degradation were determined using 25 mg and 75 mg of the K-OMS-2 sample. The percent degradation of methylene blue was calculated as follows:

Degradation (%) = $\frac{Ao-Af}{Ao} \times 100\%$

Where A_0 and A_f are the initial and final absorbance, respectively.

3. RESULTS AND DISCUSSION

3.1 Structural analysis

The powder XRD patterns of the synthesized materials are shown in Figure 1.



Figure 1: Powder XRD patterns of the synthesized materials

The diffraction pattern of K-OMS-2 corresponded to that of synthetic cryptomelane (JCPDS file 29-1020) with peaks at 12.8, 18.5, 28.9, 37.5, 42, 50, 56.2, 60.4 and 65.5° in the 20 range [20]. The diffraction patterns of the doped K-OMS-2 materials were similar to that of K-OMS-2 with no observable difference in the shape, position and intensity of the peaks. Moreover, diffraction patterns of doped K-OMS-2 materials did not contain any additional peaks suggesting that dopant cations were incorporated in the structure of K-OMS-2 without the formation of segregated dopant oxides or other impurities [20, 21]. The synthesized materials, therefore, contain the tetragonal unit cell and belong to the I4/m (C54h) space group [22, 23].

The FT-IR spectra of the synthesized materials are shown in Figure 2 (a-e).



Figure 2: FT-IR spectra of (a) K-OMS-2 (b) V-K-OMS-2 (c) V-Cu-Co-K-OMS-2 (d) V-Cu-Fe-K-OMS-2 (e) V-Cu-Ni-K-OMS-2

Muya et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications The spectrum of K-OMS-2 exhibited absorption bands at 463 cm⁻¹, 531 cm⁻¹, 717 cm⁻¹, 1633 cm⁻¹ and 3443 cm⁻¹. The peaks at 463, 531 and 717 cm⁻¹ were characteristic vibrations of the octahedral framework of cryptomelane [24, 25]. The peak at 1633 cm⁻¹ was attributed to the bending vibrational mode of water molecules in the tunnels of the K-OMS-2 materials [24, 26]. The broad band at 3443 cm⁻¹ was attributed to the stretching vibrational modes of hydroxyl groups of water molecules adsorbed on the surface of K-OMS-2 [24, 27]. The spectra of doped K-OMS-2 materials exhibited absorption bands characteristic of cryptomelane framework. However, on doping K-OMS-2 with vanadium (V-K-OMS-2) the characteristic absorption bands shifted to higher frequencies (535, 576 and 719 cm⁻¹) relative to those of K-OMS-2 suggesting incorporation of the heavier V atoms in the frame work of cryptomelane. In addition, significant changes in the relative intensities of the peaks in multi-doped K-OMS-2 octahedral framework [12].

3. 2 Textural properties

A representative adsorption/desorption isotherm of K-OMS-2 is shown in Figure 3.





All the synthesized materials exhibited type II adsorption isotherms [7]. In addition, the synthesized materials exhibited type 3 hysteresis associated with mesoporosity due to aggregation of nanoparticles with rod-like morphology [29].

The textural properties of the synthesized materials are summarized in Table 1.

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Sample	Surface Area	Pore size	Pore volume
K-OMS-2	69.1	3.6	0.18
V-K-OMS-2	94.9	5.3	0.25
V-Cu-Co-K-OMS-2	162.4	5.3	0.35
V-Cu-Fe-K-OMS-2	102.58	5.4	0.23
V-Cu-Ni-K-OMS-2	73.0	5.2	0.19

 Table 1: Textural properties of the synthesized materials

Doped K-OMS-2 samples had higher BET surface areas and pore volumes than K-OMS-2 presumably due to structural distortions and morphological changes (*vide infra*) attributable to incorporation of dopants in the framework of K-OMS-2 [30].

3.3 Morphological properties

The FE-SEM micrographs of the synthesized materials are as shown in Figure 4.



Figure 4<u>1</u>: The FE-SEM micrographs of: (a) K-OMS-2, (b) V-K-OMS-2, (c) V-Cu-Co-K-OMS-2, (d) V-Cu-Fe-K-OMS-2, (e) V-Cu-Ni-K-OMS-2

The K-OMS-2 micrograph shows the typical fibrous morphology of the catalyst [31]. The fibrous morphology indicates the anisotropic growth behavior of K-OMS-2 materials [32]. The length of

Muya et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications the nanofibres decreased significantly on doping K-OMS-2 to form irregular aggregated nanoparticles. The change in morphology suggests that the dopant cations were incorporated into the framework of K-OMS-2 [10] and is consistent with the high surface area and pore volumes of the doped K-OMS-2 materials.

3.4 Elemental Analysis

The elemental composition of the synthesized materials is shown in Table 2.

Catalyst	Mn%	K%	V%	Co%	Fe%	Cu%	Ni%	S%
K-OMS-2	94.4293	4.808	-	-	-	-	-	0.6172
V-K-OMS-2	89.7016	4.8674	4.8988	-	-	-	-	0.3435
V-Co-Cu-K-OMS-2	86.0913	4.9249	5.0049	1.895	-	1.2076	-	0.3762
V-Fe-Cu-K-OMS-2	85.9027	4.6902	4.7803	-	2.2086	1.7467	-	0.4037
V-Ni-Cu-K-OMS-2	86.2441	4.7106	4.9522	-	-	1.6868	1.499	0.3121

 Table 2: Elemental composition of synthesized materials

The K-OMS-2 sample was primarily composed of manganese and potassium with residual amount of sulphur from adsorbed manganese sulphate precursor. The pentavalent vanadium cations were successfully doped in the K-OMS-2 materials. However, the amounts of divalent cations incorporated in the K-OMS-2 samples were significantly lower than theoretical amounts from the synthesis, with the exception of iron. The amount of manganese decreased on doping K-OMS-2 suggesting framework substitution rather than replacement of potassium and water molecules in the tunnels by dopants [33]. Doped K-OMS-2 materials also contained small amounts of sulphur from adsorbed sulphate precursors.

3.5 Thermal Analysis



The TGA data of the synthesized materials is shown in Figure 5.

Figure 5: The TGA curves of: (a) K-OMS-2, (b) V-K-OMS-2, (c) V-Cu-Co-K-OMS-2, (d) V-Cu-Fe-K-OMS-2, (e) V-Cu-Ni-K-OMS-2

The TGA profiles of K-OMS-2 and doped K-OMS-2 samples exhibited four major weight losses. These weight losses occurred between 25-350°C, 350-520°C, 520-620°C and 620-700°C. The first weight loss was attributed to the loss of physisorbed water [34, 31]. The second weight loss was due to evolution of chemisorbed water and active oxygen species from the synthesized materials [35, 7].

Muya et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications The two distinct weight losses between $520-620^{\circ}$ C and $620-700^{\circ}$ C were attributed to evolution of structural oxygen due to transformation of cryptomelane to bixbyite (Mn₂O₃) and hausmannite (Mn₃O₄), respectively [34,31,36]. The first and second weight losses of K-OMS-2 are lower than those of doped materials, suggesting lower concentration of sorbed species, presumably due to the lower surface area and fibrous morphology of K-OMS-2 [37]. The third and fourth percent weight losses of doped samples are significantly higher than those of K-OMS-2 indicating that K-OMS-2 is more thermally stable. This is attributed to presence of lattice vacancies and structural distortions due to differences in the ionic sizes of manganese and dopant cations [12, 35].

3.6 Degradation of Methylene Blue

The percent decrease in the concentration of methylene blue with time using the synthesized materials is shown in Figure 6.





There was no observable degradation methylene blue in the absence of the catalysts even after 1 h. The highest degradation of 64.67 and 82.35% after 10 and 30 min, respectively, was obtained with the V-Cu-Co-K-OMS-2 sample. The K-OMS-2 sample also exhibited good degradation of 56.81% after 10 min and 81.22% after 30 min. The V-Cu-Ni-K-OMS-2 sample was the least effective with 16.4 and 26.63% degradation after 10 and 30 min, respectively. The K-OMS-2 sample, with the smallest surface area and pore volume, exhibited the second highest percent degradation suggesting that textural properties are not the major determinant in decomposition of methylene blue. Similar results were obtained by Sriskandakumar and co-workers, who correlated the degradation of methylene blue with the oxidation states of the dopants and average manganese oxidation states of

Muya et al RJLBPCS 2019 www.rjlbpcs.com manganese in K-OMS-2 and doped K-OMS-2 materials [18].

4. CONCLUSION

K-OMS-2 and doped K-OMS-2 materials were successfully synthesized using the reflux method. The synthesized materials were highly crystalline with diffraction patterns corresponding to those of synthetic cryptomelane. Characterization data suggests that the dopants were incorporated into the framework of K-OMS-2 without formation of segregated dopant oxides. The incorporation of the high valence V⁵⁺ cations into doped materials was almost quantitative but incorporation of low valence cations was significantly less than theoretical amounts. Incorporation of dopants in the K-OMS-2 framework decreased the thermal stability and caused significant reduction in the size of the nanofibres from ca. 500 nm to ca. 100 nm with consequent increase in the surface areas of doped K-OMS-2 materials. However, the synthesized materials were thermally stable under typical adsorption and catalytic conditions. The rate of degradation of methylene blue increased with the amount of catalyst and time. V-Co-Cu-K-OMS-2 was the most effective catalyst with 82.35% degradation while V-Ni-Cu-K-OMS-2 was the least effective with 26.63% degradation after 30 min. Thus, V-Co-Cu doped K-OMS-2 is a promising catalyst for degradation of methylene blue blue dye.

CONFLICT OF INTEREST

The authors have no conflict of interest.

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