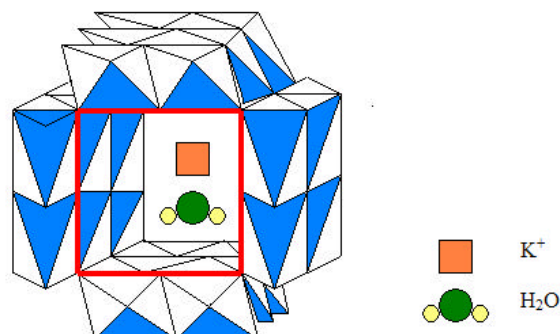


*Naftali N. Opembe, Young-Chan Son, Thamayanthy Sriskandakumar and Steven L. Suib.*

**Kinetics and Mechanism of 9H-Fluorene Oxidation Catalyzed  
by Manganese Oxide Octahedral Molecular Sieves**

## 1.0 Structure of OMS-2 catalyst.



**Figure 1.** Structure of OMS-2

The catalyst used in this oxidation study belongs to a class of synthetic manganese oxides with a tunnel structure, called octahedral molecular sieves (OMS). Synthetic OMS catalyst has a one-dimensional tunnel structure formed by a 2 5 2 edge shared MnO<sub>6</sub> octahedral chains, labeled OMS-2 (Figure 1). The tunnels have dimensions of 4.6 Å 5 4.6 Å, and the overall composition is KMn<sub>8</sub>O<sub>16</sub>.*n*H<sub>2</sub>O. In the as-synthesized form the tunnels contain exchangeable potassium ions and some water molecules.

## **2.0 Experimental Section**

### **2.1 Synthesis of OMS-2 Catalysts.**

OMS-2 materials were synthesized according to literature methods. Some of the synthetic routes utilized are: reflux method, solvent free method, hydrothermal method, and the constant frequency microwave technique. These methods are briefly highlighted below.

### **2.2 OMS-2 by Reflux Method (OMS-2<sub>R</sub>)**

In a 500-mL round-bottom flask with condenser, 225 mL of potassium permanganate solution (0.4 M) was added to a mixture of 67.5 mL of manganese sulfate hydrate solution (1.75 M) and 6.8 mL of concentrated nitric acid. The dark brown slurry was refluxed for 24 h, then filtered and washed with distilled de-ionized water (DDW) several times until the pH was ~7.0. The catalyst was dried at 120 °C overnight before use.

### **2.3 OMS-2 by Hydrothermal Method (OMS-2<sub>H</sub>)**

In the hydrothermal method (OMS-2<sub>H</sub>), 9.48 g (0.06 mol) of KMnO<sub>4</sub> and 22.05 g (0.09 mol) of Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O (stoichiometric ratio of KMnO<sub>4</sub>:Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O = 2:3) powders were dissolved in distilled de-ionized water so as to maintain the same molar ratios. The mixture were then placed in Teflon vessels, enclosed into constant pressure Parr autoclaves and maintained at 100 °C for 24 h. The precipitate was thoroughly washed with distilled deionized water several times to remove any ions, which may remain in the product, and finally dried at 80 °C in air overnight.

## 2.4 OMS-2 by Solvent free technique (OMS-2<sub>S</sub>)

In the solvent free technique (OMS-2<sub>S</sub>), 9.48 g (0.06 mol) of KMnO<sub>4</sub> and 22.05 g (0.09 mol) of Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O (stoichiometric ratio of KMnO<sub>4</sub>:Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O = 2:3) powders were mixed and ground homogeneously in an agate mortar. The mixed powders were then placed in a capped glass bottle and maintained at 80 °C for 4 h. The resulting black powder was thoroughly washed with distilled deionized water several times to remove any ions which may remain in the product, and finally dried at 80 °C in air overnight.

## 2.5 OMS-2 by Microwave technique (OMS-2<sub>MW</sub>)

In the microwave method (OMS-2<sub>MW</sub>), 9.48 g (0.06 mol) of KMnO<sub>4</sub> and 22.05 g (0.09 mol) of Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O (stoichiometric ratio of KMnO<sub>4</sub>:Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O = 2:3) powders were dissolved in distilled de-ionized water so as to maintain the same molar ratios. The mixture were then placed in Teflon autoclave and maintained at 120 °C for 4 h. The precipitate was thoroughly washed with distilled deionized water several times to remove any ions, which may remain in the product, and finally dried at 80 °C in air overnight.

## 2.6 Ion-exchange

OMS-2<sub>B</sub> was ion-exchanged to give the H<sup>+</sup> form. The exchanged material was labeled <sup>H</sup>OMS-2<sub>B</sub>. The strategy employed towards this end utilized NH<sub>4</sub><sup>+</sup> followed by thermolysis to reduce NH<sub>4</sub><sup>+</sup> to H<sup>+</sup>. OMS-2 was added to a 25 mL solution of 20 % (w/v) solution of ammonium nitrate and stirred at room temperature for 3 h. After the slurry was allowed to settle, the clear liquid phase was decanted and another portion of 25 mL ammonium nitrate was added and further stirred for 3 h. The slurry was filtered and

washed thoroughly until neutral to a pH paper. The residue was dried at room temperature before being calcined at 400 °C in air for 8 h.

### 3.0 Characterization.

#### 3.1 X-ray Diffraction Studies (XRD)

The as-synthesized OMS-2<sub>B</sub> and other OMS-2 catalysts were characterized using powder X-ray diffraction (XRD) methods. A Scintag XDS-2000 diffractometer with a Cu K $\alpha$  radiation and a beam voltage of 45 kV and 40 mA of beam current was used. The data were collected in the 2 $\theta$  range of 5-75 °C. The pattern thus obtained was identified using the JCPDS database and the materials were found to be pure (Figure 2). Crystallites sizes were calculated applying Scherrer's equation (Equation 1) to the diffraction peaks at 2 $\theta$  = 28.8° and 49.8°. Instrumental line broadening was corrected using a LaB<sub>6</sub> standard.

$$L, \text{ thickness} = 0.94 \lambda / (B \cos \theta) \quad [1]$$

where  $\lambda = 1.54 \text{ \AA}$

$$B = B_{\text{actual}} = \sqrt{B_{\text{observed}}^2 - B_{\text{resolution}}^2}$$

$$\theta = 28.8^\circ \text{ and } 49.8^\circ$$

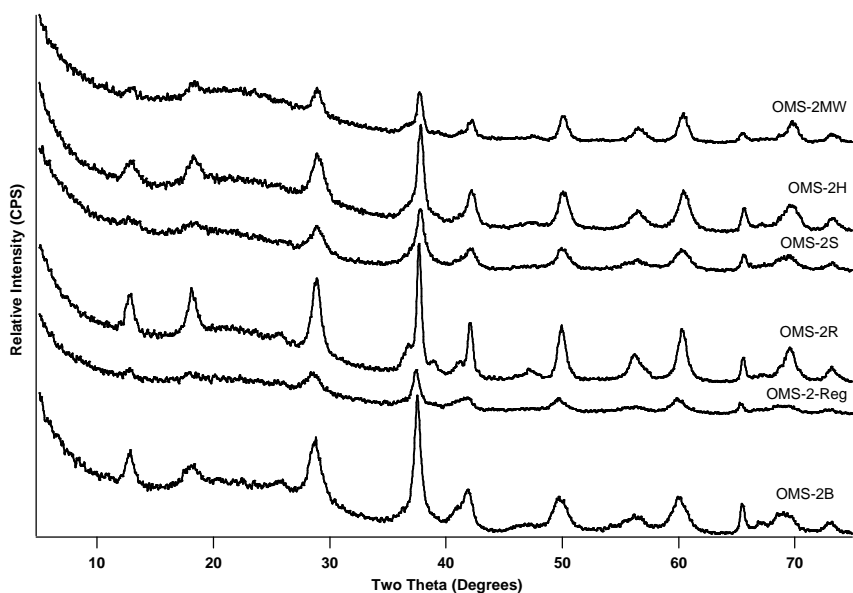
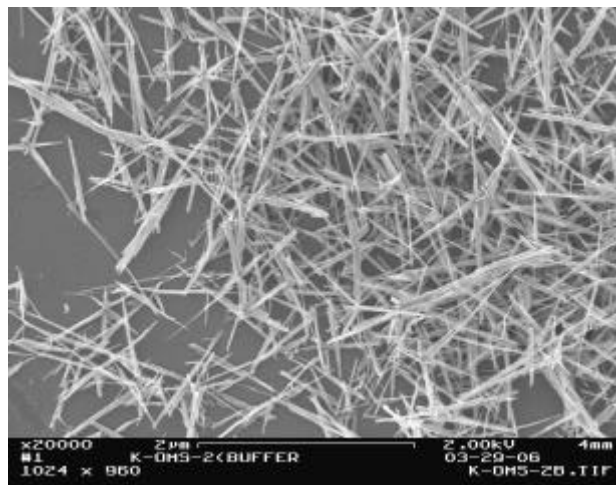


Figure 2. X-ray diffraction patterns of variously synthesized OMS-2 catalysts where: OMS-2<sub>B</sub> refers to reflux under acidic buffer conditions, OMS-2-Reg refers to regenerated OMS-2<sub>B</sub>, OMS-2<sub>R</sub> refers to acidic reflux method, OMS-2<sub>H</sub> refers to hydrothermal methods, OMS-2<sub>S</sub> refers to solvent free technique and OMS-2<sub>MW</sub> under a microwave field.

### 3.2 Morphology

The morphology of the catalysts was studied by scanning electron micrographs taken on a Zeiss DSM 982 Gemini field emission scanning electron microscope (FESEM) with a Schottky Emitter at an accelerating voltage of 2 kV and a beam current of 1  $\mu$ A. The SEM images in Figure 3 show a needle-like morphology with particles sizes of a few tens of nanometers.



**Figure 3:** Field Emission Scanning Micrograph Image of OMS-2<sub>B</sub>

### **3.3 Average oxidation state (AOS)**

The average oxidation state of the as-synthesized OMS-2<sub>B</sub> in the states Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup> was determined by the potentiometric titration method. The catalyst was dissolved in concentrated hydrochloric acid so as to convert all the manganese into Mn<sup>2+</sup>, and titrated to Mn<sup>3+</sup> complex by sodium pyrophosphate versus potassium permanganate. This gave the total Mn content, based on which AOS was determined by reducing the solid to Mn<sup>2+</sup> by ferrous ammonium sulfate and back titrating the excess Fe<sup>2+</sup> by the permanganate standard.

### **3.4 Surface area Measurements**

Specific surface area was determined by nitrogen sorption. This was done at 77K with a Micrometrics ASAP 2010 instrument. The samples had to be degassed first at 120 °C for slightly more than 2 h. The surface area of the samples was determined by the Brunauer-Emmett-Teller (BET) method.



#### 4.0 Kinetic isotope Effect (KIE)

The kinetics of oxidation of fluorene-d10, a deuteriated form of 9H-fluorene, were carried out and the results compared to those of 9H-fluorene. All the reactions were exposed to the same conditions and timed, with periodic sampling, for approximately the first 30 minutes. These results are given in Figure 4. Equations (2) and (3) can be used to describe these kinetics merely switching the substrate from 9H-fluorene to fluorene-d10 in equations 2 and 3:

$$\text{Rate} = k [\text{9H-fluorene}]^\alpha [\text{O}_2]^\beta \text{ and} \quad [2]$$

$$\text{Rate} = - d (\text{9H-fluorene})/d (t) \quad [3]$$

Where  $k$  stands for the rate constant,  $\alpha$  and  $\beta$  represents reaction orders with respect to 9H-fluorene and oxygen respectively, and  $t$  stands for time.

For this reaction, since the oxygen participating in the reaction is dissolved oxygen, its concentration is perceived to be constant throughout the reaction, hence equation (2) can be rewritten to give equation (4). A high catalyst loading and a linear plot also lead to the assumption that the reaction is pseudo-first order with the only variable being the substrate.

$$\text{Rate} = k' [\text{9H-fluorene}]^\alpha \quad [4]$$

Where  $k'$  represents  $k [\text{O}_2]^\beta$

Combining equations (3) and (4) and after a calculus operation yields equation (5) below.

$$\text{Ln} [\text{9H-fluorene}]_t = - k' t + \text{Ln} [\text{9H-fluorene}]_o \quad [5]$$

A plot of  $\text{Ln} [\text{9H-fluorene}]_o / [\text{9H-fluorene}]_t$  vs. time ( $t$ ) is shown in the kinetic isotope effect graph (KIE).

## 5.0 Other characteristics of OMS-2 catalysts

**Table 1.** Characteristics of OMS-2 materials synthesized under different conditions.

Entry	<sup>[a]</sup> L.A (mmol/g) STP	Surface area (BET) (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Percent Mesopore volume. (%)
1	0.61	62	0.38	98
2	0.70	90	0.46	63
3	0.63	70	0.27	85
4	0.98	156	0.52	92
5	0.75	80	0.49	98

Entries refer to OMS-2 catalysts prepared under different methods where 1 refers to reflux under acidic buffer conditions (OMS-2<sub>B</sub>), 2 refers to acidic reflux methods (OMS-2<sub>R</sub>), 3 refers to hydrothermal methods (OMS-2<sub>H</sub>), 4 solvent free (OMS-2<sub>S</sub>) and 5 under a microwave field (OMS-2<sub>MW</sub>) [a] Lewis acidity.