Photo-catalytic selective organic transformations by Fe-doped octahedral molecular sieves (manganese oxide) nano-structure

S. Said, Heba H. El Maghrabi, M. Riad and S. Mikhail
Catalysis Department, Refining Division, Egyptian Petroleum Research Institute, Cairo, Egypt

ABSTRACT
The future development of chemistry entails environment-friendly and energy-sustainable alternatives for organic transformations. Visible light photo-catalysis can address these challenges. Octahedral molecular sieve manganese oxide (cryptomelane, OMS-2) and Fe-doped OMS-2 nano-structures were prepared to be used as affective visible light photo-catalysts for the oxidation of cyclohexane. The photo-catalysts were prepared by reflux method (at 100°C, for 24 h) under atmospheric pressure by using different molar ratios of Fe/Mn (0, 0.03, 0.08 and 0.10). Several techniques such as X-ray diffraction, transmission electron microscopy, Fourier-transform infrared spectra, nitrogen adsorption/desorption isotherms and thermal analysis were performed for characterizing the structure and the morphology of the prepared samples. The results revealed that the Fe-OMS-2 samples have a well-crystalline cryptomelane framework. In addition, no peaks related to the Fe dopant were detected, indicating the incorporation of Fe species into the framework of cryptomelane. The main product of photo-catalytic oxidation reaction of cyclohexane is cyclohexanone with a selectivity of 100% after 3 h for highest conversion on using 0.08Fe-OMS-2 sample.

1. Introduction
The selective oxidation of hydrocarbons involving the activation of C-C, C-H bonds and/or the concomitant formation of C-OH or C = O bonds to produce more suitable products (for fine chemical synthesis) is a must [1]. Cyclohexane oxidation products (cyclohexanol and cyclohexanone) are important reagents for the production of caprolactam, adipic acid and monomers to prepare nylon-6 and nylon-6,6.
polymers. Currently, the industrial processes for cyclohexane oxidation on using cobalt salts or metal–boric acid with molecular oxygen as an oxidant have some inherent drawbacks (lower conversion and selectivity, expensive investment) and cause serious pollutions [2].

Thus, it is important to develop effective systems with low-cost environmentally benign catalysts under milder reaction conditions to meet the challenge [3].

Concurrently, photo-catalytic synthetic processes via selective oxidation have been developed [4]. Liu et al. [5] studied the photo-catalytic degradation of polyethylene film with cryptomelane as photo-catalyst in the air under either ultraviolet and/or visible light irradiation. Iyer et al. [6] evaluated the activities of various K-OMS-2 and metal-doped K-OMS-2 catalysts prepared by different synthesis procedures. The results showed that K-OMS-2 prepared by solvent-free method had the highest activity for selective oxidation of 2-propanol to acetone under visible light irradiation. Nevertheless, selective photo-catalytic oxidation of cyclohexane in the liquid phase is of particular interest [7,8].

She et al. [9] studied the preparation of vanadium-substituted molybdophosphoric acid (PMo_{12−n}V_n, n = 1–3) samples for the selective photo-oxidation of cyclohexane in the presence of visible light and using nitrous oxide (N_2O) as a green oxidant. The results revealed that the PMo_9V_3 sample showed a higher photo-catalytic activity and selectivity toward the formation of cyclohexanone, with selectivity reaching 82.7% under optimized conditions. Otherwise, Tang et al. [10] studied the oxidation of cyclohexane on the same photo-catalyst but using dioxygen (O_2) as oxidant under visible light irradiation. The results represented that the products are mainly composed of cyclohexanol and cyclohexanone, with conversion: 8.2% and 33.3%, and selectivity: 17% and 79%, respectively.

Henríquez et al. [11] investigated the selective oxidation of cyclohexene by visible light using Fe-doped TiO_2 and bismuth oxyhalide BiOI photo-catalysts under ambient conditions. The BiOI sample showed the highest selectivity for cyclohexanol production (cyclohexanone/cyclohexanol = 0.23). The cyclohexanol yield depended linearly on the band gap of the BiOI reached the maximum cyclohexanol yield (16.5 mol m^{-2}g).

This paper intends to investigate the performance of Fe-doped OMS-2 for photo-catalytic oxidation reaction of cyclohexane at room temperature. The Fe-doped samples with different Fe/Mn molar ratios were prepared via the facile refluxing method under atmospheric pressure. The effects of Fe doping on the morphology, structure and catalytic performance were also studied.

2. Experimental procedure

2.1. Materials

For preparing the Fe-OMS-2 all the starting materials, Fe_2(SO_4)_3, MnSO_4.H_2O, KMnO_4 and acetic acid, are reagent grade of 99.9% purity.

2.2. Preparation of Fe-doped cryptomelane samples

Fe-doped cryptomelanes were prepared by adding KMnO_4 solution to mixtures of Fe_2(SO_4)_3, MnSO_4 and acetic acid at different molar ratios of Fe/Mn using the reflux method under atmospheric pressure [12]. In a typical procedure, 80 mL of 0.4375 mol/L KMnO_4 solution was heated to 60°C and poured into 100 mL mixtures of Fe_2(SO_4)_3 and MnSO_4 solutions (the molar ratio of Fe/Mn is 0, 0.03, 0.08 or 0.10). A suitable amount of 2 mol/L acetic acid was added to the mixture. The mixture was then heated and kept boiling under reflux and continuous stirring for 24 h. All samples were washed with de-ionized water, dried in an oven at 60°C for 7 days and then grounded in an agate mortar to particle sizes of 0.125 mm. After that, the products were stored in closed penicillin glass tubes at room temperature. The samples are donated according to the Fe/Mn mole ratios (0, 0.03, 0.08 or 0.10) as OMS-2, (0.03) Fe-OMS-2, (0.08) Fe-OMS-2 and (0.1) Fe-OMS-2, respectively.

2.3. Characterization methods

2.3.1. X-ray diffraction analysis (XRD)

The structure and phase purity of the prepared samples were analyzed via X-ray diffraction (XRD). The experiments were carried out using a Shimadzu XD-1 diffractometer on Cu Ka radiation (λ = 0.1542 nm) at a beam voltage of 40 KV and a beam current of 40 mA. The intensity data were collected in a 2θ range of 10–70° with a scan rate of 0.7° s^{-1}. The phase identification was made by comparing to the Joint Committee on Powder Diffraction Standards (JCPDS 29-1020). The coherent scattering domain (CSD) size of the OMS-2 and Fe-doped samples was determined from the (211) XRD peak at 2θ = 37.6° using the Scherrer equation.
2.3.2 Fourier transform infrared spectroscopy (FTIR)
FTIR was investigated on the Perkin-Elmer-Spectrum-1 spectrometer in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. The samples were ground to fine powder and dispersed in KBr to compress into pellets before measurements.

2.3.3. Thermal analysis
Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed to study the structural changes in the prepared samples with thermal treatment. A 15 mg of sample was heated up to 1000°C, with a heating rate of 10°C min⁻¹ in an air flow at a rate of 100 mL min⁻¹ on SDTQ-600 (TA-USA) thermo balance instrument.

2.3.4. Surface analysis using N₂ adsorption technique
The textural properties were determined from the N₂ adsorption–desorption isotherms at liquid nitrogen temperature (−196°C) using NOVA 3200 S Unite, automates gas sorption analyzer (Quantachrome Corporation, Hook, England) system. All samples were degassed at 250°C for 24 h in nitrogen atmosphere prior each measurement to ensure a dry clean surface. The pore size distributions were determined from the Barrett–Joyner–Halenda method applied to the desorption branch of the isotherm.

2.3.5. High-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) spectroscopy were conducted using a JEOL (Croissy-sur-Seine, France) 2100F TEM at an accelerating voltage of 200 kV. To prepare the TEM samples, a dilute particle–ethanol colloidal mixture was ultrasonicated for 30 min and a drop of solution was placed on a carbon-coated Cu TEM grid.

2.4. Photo-catalytic reaction
The optical properties of the prepared samples were performed by UV-Vis diffuse reflectance and photoluminescence (PL) (Jasco model V-570; Jasco, Essex, England) spectrophotometer at room temperature to estimate the energy band gap.

The photo-catalytic oxidation reaction of cyclohexane was carried out at room temperature, according to the following procedure: 0.05 g of the prepared sample and 10 mmole of cyclohexane were put into a 50 mL photochemical reactor, containing 10 mL of acetonitrile, fitted with a cooling jacket. The choice of acetonitrile was based on its stability toward light irradiations. Samples were then collected every 2 h after switching on the lamp for the total photo-oxidation period of 12 h. The collected samples were analyzed by gas chromatography. Reaction products were identified by comparison of their retention times with known reference compounds.

3. Results and discussion
3.1. Structural and morphology changes of the prepared samples
Figure 1 presents the XRD patterns of the undoped OMS-2 and Fe-doped samples. For undoped sample (ONS-2), the pattern detected peaks that are well in agreement with a pure cryptomelane (JCPDS 29-1020) with a tetragonal structure, $a = b = 9.78$ Å, $c = 2.86$ Å. The intense and sharp diffraction peaks appear at $2\theta = 12.9°, 18.2°, 28.9°, 37.7°, 49.9°$ and $60.5°$ assigned to the $(110), (200), (310), (211), (411)$ and $(521)$ planes, respectively. The CSD size of the OMS-2 particles (calculated according to the Scherrer equation) is 15 nm at $2\theta = 37°$.

The diffractogram for Fe-OMS-2 samples (Figure 1) clarified the appearance of peaks at the same $2\theta$ values as the undoped one and that identified as cryptomelane-type manganese oxide. Otherwise, no additional peaks attributed to Fe species appeared but with the increase in the Fe-dopant content some changes were observed in the diffraction intensities, suggesting that the iron is well incorporated and highly dispersed, and hence under the determination limit of XRD analysis [13].

On the other hand, for the molar ratios of Fe/Mn = 0.03 and 0.08, the diffraction patterns reveal an increase in peak intensity (increase in crystallinity) and a decrease in FWHM, with an increase in the CSD size (Table 1). Because the crystal radius of Fe³⁺ (0.785 Å) is higher than those of Mn⁴⁺ (0.67 Å) and Mn³⁺ (0.72 Å), the Fe species have the chance to incorporate into the OMS-2 framework structure, resulting in the observed

![Figure 1. The XRD patterns of OMS-2 and Fe-doped OMS-2 samples.](image-url)
different crystallite growth behavior [14]. On further increasing the Fe/Mn molar ratio to 0.1, a decrease in diffraction intensity and an increase in FWHM, with a decrease in CSD, occurred. This may be related to the distribution of Fe species not only in the OMS-2 framework but also into the tunnel structure. As is known, the ionic radius of Fe$^{3+}$ (0.785 Å) is significantly lower than that of K$^+$ (1.65 Å), it is difficult for Fe species to substitute K ions and so it is easy to incorporate or adsorb in the tunnel structure [15].

The TEM images of undoped (OMS-2) and Fe-OMS-2 (with different Fe/Mn molar ratios) are displayed in Figure 2. As can be seen, OMS-2 is composed of non-uniform needle-like nano-rod morphology with regular shape in which their ends are similar in diameter as their middle part. Meanwhile, upon increasing the Fe doping up to Fe/Mn = 0.1, the needle rods increased in width and decreased in length (Figure 2), resulting in the formation of grain-like aggregates of nano-particles with a rod-like morphology. The formation of this morphology was most likely due to a slight distortion of the tetragonal crystal structure that confirming the incorporation of Fe species into cryptomelane structure during the nucleation and growth processes leads to a large number of adsorption sites and thus improves the catalytic performance for the photo-oxidation reaction.

As clarified, the particle size of the (0.1)Fe-OMS-2 is small compared to the undoped one. Generally, the average crystal sizes calculated by the Scherrer equation reflect the CSD sizes of the crystals, while the TEM gives the actual physical dimensions of the crystallites. So, the difference in the particle size calculated by the Scherrer equation and that observed by TEM attributed to the disorder in the structure and the crystal shape [16].

The corresponding selected area X-ray energy disperse (SAED) pattern (inset) proves that the prepared samples are single crystalline and have a nano-rod structure lying on the (221) planes.

The FTIR spectrum of the undoped (OMS-2) and Fe-OMS-2 samples (Figure 3) showed four characteristic bands around 702, 506, 451 and 415 cm$^{-1}$ that can be assigned to the lattice vibration modes of Mn-O in [MnO$_6$] octahedra [14]. These bands present a clear signature of the cryptomelane structure. Additionally, a broad band observed at ~3338 cm$^{-1}$ is assigned to O–H stretching vibration ($\nu$ O–H) due to the presence of

| Sample       | XRD CSD (nm) | N$_2$ physique | \(V_p\) (ccg$^{-1}$) | \(D_p\) (nm) | Particle size (TEM) |
|--------------|--------------|----------------|----------------------|--------------|---------------------|
| OMS-2        | 15           | 121            | 0.28                 | 12           | 192                 |
| 0.03Fe-OMS-2 | 42           | 97             | 0.2                  | 5            | 254                 |
| 0.08Fe-OMS-2 | 43           | 107            | 0.24                 | 6            | 277                 |
| 0.1Fe-OMS-2  | 27           | 115            | 0.25                 | 5            | 266                 |

Figure 2. TEM images, the corresponding SAED patterns and EDX patterns of OMS-2 and Fe-doped OMS-2 samples.
hydroxyl as well as both adsorbed and tunnel water molecules. The bending mode of H\textsuperscript{+}–O–H from H\textsubscript{2}O was observed at 1619 cm\textsuperscript{−1}, which confirmed the presence of water in the 2 × 2 tunnel structure. Upon doping of Fe into OMS-2 structure, the bands at 415, 451, 506 and 702 cm\textsuperscript{−1} shifted to 465, 513 and 693 cm\textsuperscript{−1}; 464, 513, 538 and 710 cm\textsuperscript{−1} and 460, 530, 538 and 710 cm\textsuperscript{−1} for (0.03) Fe, (0.08) Fe and (0.1) Fe-OMS-2, respectively. Moreover, the peak intensities at 702, 506, 451 and 415 cm\textsuperscript{−1} significantly decreased with increasing Fe doping content, indicating the change of Mn-O vibrations in octahedral environments after Fe doping. In addition, a peak detected at ~1050 cm\textsuperscript{−1} (marked with an up arrow) is attributed to the vibration of Fe-O bond. The intensity of this peak increases along with the Fe doping increase up to (0.08%). This result established the existence of dispersed iron oxide species, on (0.8) Fe-OMS-2 sample (which cannot be detected by XRD analysis). On the other hand, the intensity of this peak is diminished on further increase in Fe doping to (0.1%). Otherwise, iron is not present as isolated species but most of iron atoms are incorporated in the OMS framework structure, and consequently the Fe-O vibration band is diminished, in agreement with the observed results of particle growth behavior.

For the (0.08) Fe-OMS-2 sample, a shoulder observed at 2975 cm\textsuperscript{−1} (marked with a black dot) be assigned to hydrogen bonds between water and Fe-O species. Whereas, the broad band appeared at ~3368 cm\textsuperscript{−1} becomes more intense for (0.03 and 0.08) Fe-OMS-2 samples, compared with undoped and (0.1) Fe-OMS-2 ones, indicating a considerable increase in the hydroxyl group amount.

To examine the surface area, as well as the pore size distribution, nitrogen adsorption/desorption isotherm was conducted on OMS-2 and Fe-OMS-2 prepared samples as shown in Figure 4. The textural parameters of the prepared samples are listed in Table 1. It was found that the doping of Fe has a significant impact on the surface areas, pore volume and average pore diameter of the OMS-2.

All the prepared samples exhibit characteristic type II N\textsubscript{2} adsorption–desorption isotherms (Figure 4(a)), with a hysteresis loop of type H3 according to the IUPAC classification, which is usually associated with the adsorption on aggregates of particles with a rod-like fiber morphology, forming slit-like pores [17], in agreement with TEM image (Figure 2). It is clear that the shape of the isotherms was almost unchanged upon Fe doping, indicating the preservation of the cryptomelane tunnel structure, while the N\textsubscript{2} uptake seems to decrease gradually in the order of OMS-2 > (0.03) Fe-OMS-2 > (0.1) Fe-OMS-2 > (0.08) Fe-OMS-2. Hence, the BET surface area and the total pore volume followed the same order, indicating less
accessibility of surface of (0.08) Fe-OMS-2 sample for N₂ molecules. The pore size distribution curves (Figure 4(b)) of the prepared samples show one broad peak for the undoped and low iron content (0.03Fe-OMS-2) samples, indicating a uniform meso-pores size with an average pore diameter of 17 nm. According to the TEM image (Figure 2), the agglomeration of the nano-needle bunches exhibited meso-pores between the needles, which are responsible for the high average pore diameter of pure cryptomelane sample. For (0.08) and (0.1) Fe-OMS-2 samples, the PSD curves behave like a bi-model pore size distribution which demonstrates the presence of heterogeneous meso-pores; a group of narrower meso-pores starts to appear with a pore diameter of 5 nm besides the meso-pores of OMS-2 with D = 17 nm. For (0.8) Fe-OMS-2 sample, the pore at a diameter of 17 nm is shifted to a narrow one at a diameter of 12 nm. The created narrow pore may be resulted from the assembly of the extra framework of Fe oxide particles, which are loosely coherent, in agreement with FTIR spectrum. This result provokes that the iron doping into OMS-2 alters the substitution behavior of Mn by Fe but coherent iron oxide species are formed. S_{BET}, total pore volume and pore diameter of OMS-2 are decreased upon iron doping. This criterion may be resulted from either the incorporation of some Fe species into the OMS-2 structure or other coherent iron ones accumulated inside the pores, leading to shrinking in the pore abundance and hence a decrease in the surface area (as estimated from the pore size distribution curves).

From the TGA profile of the prepared sample (Figure 5), three major weight losses could be observed between 50°C and 1000°C. The first weight loss (about 10%, up to 250°C) is owing to the desorption of the physisorbed and chemically adsorbed water. The second weight loss (about 3%) occurs at 580°C, may be due to the elution of lattice oxygen species of the materials [18], indicating that the tunnel structure of the OMS-2 is not stable. When the temperature is over 780°C, the prepared cryptomelane sample starts to lose lattice oxygen from the framework structure and decomposes into the Mn₂O₃ phase [19]. These thermal changes are consistent with its DTA profile (Figure 5): it displayed one exothermic peak at 253°C and two endothermic peaks located at 583°C and 860°C. The intense exothermic peak at 253°C is associated with the crystallization steps for the formation of cryptomelane phase [20]. All the thermal processes related to the desorption of structural oxygen close to the surface,

Figure 5. TGA and DTA curves of OMS-2 and Fe-doped OMS-2 samples.
and oxygen depletion from the structure of the material and its decomposition to bixbyte (Mn$_2$O$_3$) phase are well correlated with the endothermic peaks at 583°C and 860°C. Upon doping of Fe into OMS-2 structure, the exothermic peak detected at 253°C (Figure 5) becomes shallow and diffuses as Fe content increases; this can be explained by $\Delta H$ value due to the formation of crystalline cryptomelane phase thermal event. It is found that $\Delta H$ values decreased as doping of Fe increased (194, 172, 62 and 13 J/g) for OMS-2, (0.03) Fe-OMS-2, (0.08)Fe-OMS-2 and (0.1) Fe-OMS-2, respectively. This means that the crystallization steps for the cryptomelane formation become effortless with Fe doping. Besides, the endothermic peak observed at ~581°C is more pronounced as Fe/Mn increases. The $\Delta H$ value of the elution of lattice oxygen process decreases in the order of OMS-2 (11 J/g) > (0.03) Fe-OMS-2 (9 J/g) > (0.08)Fe-OMS-2 (4 J/g) > (0.1)Fe-OMS-2 (3 J/g). The weight losses (TGA profile) are 3% for OMS-2, 4% for (0.08) Fe-OMS-2 and 5% for (0.1)Fe-OMS-2, which suggest that the presence of Fe in the cryptomelane structure promotes the mobility and availability of the lattice oxygen, in comparison to undoped sample.

3.2. Photo-catalytic oxidation reaction

As is known, OMS-2 nano-rods have high ability for light absorption in the range of 300–800 nm [21]. The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) of the undoped and Fe-OMS-2 samples is shown in Figure 6. The absorption spectra indicate a broad absorption band, suggesting that the prepared samples have perfect ability in light absorption and are demonstrated to be efficient photo-catalysts which may be due to the variations in the valence of Mn ions, and the contents of water and K$^+$ in the structure of OMS-2 [22]. Further, in the whole Fe-doping range, the reflectance of the doped OMS-2 is higher than that of the undoped one, indicating that Fe doping greatly enhances the light absorption in visible range follow up the strongest ability in photooxidation activity. Light absorption properties of Fe-OMS-2 samples may be affected by the following:

- The insertion of exotic cations into the framework of OMS-2 will induce structural defects, such as vacancies [23,24]. These structural defects will promote the separation of photo-induced electrons and holes, hindering the recombination of these charge carriers, increasing the concentration of the photo-induced electrons and then improving the reactivity for the photo-catalytic reactions [25].

The transition of the occupied electrons on O (2p) of the Mn oxides to the unoccupied orbits (Mn (3d)) is responsible for the absorption in the visible light range and for the optical band gap energy [26]. The band gap energy $E_g$ for the prepared samples was estimated using the Kubelka–Munk function to plot the product of the square root of the absorption coefficient and the photon energy against the incident photon energy ($h\nu$) [27]. A straight line in a photon energy range close to the absorption threshold can be fitted, as shown in Figure 7. OMS-2 nano-rods have an indirect electronic transition near the band gap [28].

PL study spectra of the prepared samples were recorded and are shown in Figure 8. All samples

![Figure 6. UV-vis diffuse reflectance spectroscopy of prepared samples.](image-url)
exhibit broad emission band between 430 and 450 nm, which is ascribed to surface defects. Furthermore, the emission intensity of the undoped nano-structure sample was approximately twice that of their doped, which attributed to better crystallization caused by iron doping, as verified by the XRD and TEM results. A broad emission band of lower intensity centered at 440 nm was also recorded (Figure 8); such a band is often connected with structure defects or ionized vacancies.

The photo-catalytic oxidation reactions of cyclohexane using the prepared undoped (OMS-2) and Fe-OMS-2 samples were performed at room temperature.

Blank reactions carried out without both the prepared samples and the light irradiation show almost no conversion, which implies that the photo-oxidation reaction cannot proceed in the absence of either the light irradiation or a photo-catalyst.

The undoped (OMS-2) and Fe-OMS-2 samples were evaluated under visible light irradiation for photo-oxidation of cyclohexane, as shown in Figure 9. For the undoped sample the conversion is only 2.62 after 6 h, while Fe-OMS-2 samples show remarkably high visible-light photo-catalytic activity, indicating that Fe doping on OMS-2 has a significant impact on the catalytic behavior.
As clarified, the doping of Fe plays a decisive role on the selective catalytic oxidation process of cyclohexane to produce only cyclohexanone as demonstrated in Figure 10. It reveals that conversion efficiency grows with rising irradiation time. The low conversion of cyclohexane at first indicates a short induction period, which most likely related to initiation of the radical reaction. After 3 h reaction, a highest conversion efficiency of 20.3% was established, followed by steady state through 4 h, the cyclohexanone selectivity attained 100%. A possible explanation for this phenomenon is a radical-type autoxidation process with oxygen vacancies on (0.08) Fe-OMS-2 sample consumed evidently after 4 h irradiation reaction.

The molecular oxygen was used as an oxidant in this selective catalytic reaction. It can play an important role in fasting and increasing the combination of the cyclohexyl radicals with oxygen molecules to yield the more mobile product cyclohexanone (Figure 11). An increase in cyclohexane conversion observed at prolonged reaction times, it is logical to conclude that cyclohexane can be transformed to cyclohexanone via a simple oxidation process as the reaction proceeds. In this case, the main and the only product is cyclohexanone, which means a selectivity of 100% (Figure 11). In addition, the photo-catalytic oxidation rate (in the presence of oxygen) is almost 1.5 times more than that in the absence of oxygen under the same experimental conditions.

The effects of the amount of samples on the yield of the cyclohexanone product under the photo-oxidation of cyclohexane were studied and the obtained results are represented in Figure 12. The cyclohexane conversion was increased continuously with the increase in
sample weight from 10 to 70 mg, i.e. an increase from ~4% to ~54%, whereas the selectivity of the prepared undoped and Fe-doped catalysts toward the formation of cyclohexanone reached 100% at any point.

3.3. The mechanism study

Thus, it can be emphasized that the doping of Fe into the framework is crucial for the improvement of the catalytic performance of OMS-2. This is principally due to the structure highly stabilized by the tunnel K⁺ ions, whereas the manganese vacancies formed by the doping of Fe cations may prevent the growth of cryptomelane crystals along the c-axis direction. Although the c-axis growth was significantly suppressed, the local crystallinity was intrinsically preserved, as evidenced by XRD and TEM analyses. As a result, grain-like aggregates of nano-crystals of Fe-OMS-2 were formed; such morphology possibly provides a large number of catalytically active surface sites in Fe-OMS-2, like vacancy sites, effective for the oxygenation, that is, electron transfer from the substrate to the catalyst and from the reduced catalyst to O₂.

Combining all of the information presented herein, a mechanism for cyclohexanone formation can be proposed (Figure 13). After adsorption of cyclohexane and the initial activation by light, the photo-generated electrons may immediately transfer to Fe ions, leaving holes on the OMS-2. The occupied electrons on O (2p) of the Mn oxides are excited to the unoccupied orbits “mainly Mn (3d)” with the photo-induced active oxygen species to produce superoxide radicals O₂⁻, resulting in the effective separation of e⁻ and h⁺.
The $\text{Fe}^{2+}$ species, created from $\text{Fe}^{3+}$ by electron trapping, easily release and transfer the electron to oxygen molecules onto the surfaces of OMS-2 to produce also superoxide radicals $O_2^-$.2.

The holes in the valence band react with tunnel water molecules to produce hydroxyl radicals; a reaction occurs between an activated hydroxyl group and cyclohexane, yielding water and an adsorbed cyclohexyl radical. In agreement with the explanation of Zhong et al. [29], who correlated the photo-oxidation reaction mechanism on V-doped titanium silicate (TS-1) via hydroxyl radicals and superoxide radicals $O_2^-$.31

Xiao et al. [30] studied the photo-oxidation of cyclohexane on graphene oxide–Ag nanocrystals under solar light irradiation, and correlated the reaction mechanism with the generated hydroxyl radicals which were detected by terephthalic acid PL probing assay. In addition, Ghugal et al. [31] demonstrated that the active species responsible for the photo-degradation reaction are photogenerated electron ($e^-$), hydroxyl radical (OH$^-$), superoxide radical anion ($O_2^-$) and photogenerated holes (h$^+$). This system was found to be stable and suitable for prolonged photocatalytic application.

Subsequently, recombination of the cyclohexyl radical and the surface $O_2^-$ anion results in the formation of a peroxide intermediate that subsequently decomposes into cyclohexanone and restores the hydroxyl group on the catalyst surface.

Ma et al. [15] demonstrated surface species of Fe-doped cryptomelane X-ray photoelectron spectroscopy (XPS), i.e. the lattice oxygen ($O_2^-$) and the surface adsorbed oxygen. In addition, the increase in average oxidation state and the oxygen vacancies upon iron doping were investigated by extended X-ray absorption fine Structure spectroscopy analyses.

4. Conclusions

From the previous results, it can be concluded that iron ions were anchored into the structure of OMS-2 with the different molar ratios (Fe/Mn = 0, 0.03, 0.08 and 0.1). It was revealed that the doping of Fe plays a decisive role on the catalytic behavior of the selectively catalyzed oxidation process of cyclohexane to main product, which is only cyclohexanone. The photo-catalysts were successfully prepared through the simple reflux method, and the (0.08) Fe-OMS-2 showed the highest photo-catalytic activity compared to the other
ones. The significant enhancements in photo-catalytic performance can be attributed to the efficient separation of the electron–hole pairs. The PI study indicated the reduced recombination rate, which leads to the superior photo-oxidation efficiency under the visible light irradiation. Furthermore, photo-catalytic mechanism investigations demonstrate that superoxide radicals (O$_2^−$) play the key role in the photo-catalytic reaction. Thus, the present study offers a facile and efficient photo-catalyst for organic transformations in the near future.

**Highlights**

- Fabrication of Fe-doped cryptomelane nanostuctures has a well-crystalline cryptomelane framework.
- Achieved Fe (III) is incorporated into the framework of cryptomelane by replacing some Mn(III).
- Enhancing the photocatalytic efficiency for photo-oxidation of cyclohexane.
- The main product of catalytic cyclohexane oxidation is cyclohexanone with a selectivity of 100%

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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