

Decomposition of Pinacyanol Chloride Dye Using Several Manganese Oxide Catalysts

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The decomposition of the cyanine dye, pinacyanol chloride, has been studied using hydrogen peroxide and several mixed valent manganese oxide catalysts in aqueous, alkaline solution at room temperature. These catalysts belong to a class of porous manganese oxides known as octahedral molecular sieves (OMS). The most active catalysts were those of Fe³⁺-, Cr³⁺-, and Co²⁺-doped OMS-2. Rates of reaction were found to be first-order with respect to the dye. The highest reaction rates were observed when no H₂O₂ was present. Reactions were studied at pH = 6–11, which caused variations in the catalytic activity. The decomposition of the dye was examined using varying amounts of the catalysts, which showed the dye decomposing activity to be proportional to the amount of catalyst. X-ray diffraction studies showed that no changes in the catalyst structure occurred, implying that these reactions are surface controlled.

I. Introduction

We have reported on the synthesis, characterization, electrical, and catalytic properties of several octahedral molecular sieves (OMS) and octahedral layered (OL-1) mixed valent manganese oxides.^{1–6} These materials consist of edge- and corner-sharing MnO₆ octahedra that have tunnels on the order of molecular dimensions. The structures and composition of OMS and OL-1 materials are shown in Figure 1. OMS-1 has a 3 × 3 tunnel structure composed of triple chains of edge-shared MnO₆ units with corner-sharing of the chains and a tunnel diameter of 6.9 Å. OMS-1 is structurally related to the mineral todorokite.

OMS-2 has a 2 × 2 tunnel structure and contains a slightly smaller pore size (6.9 Å). Cations can occupy the tunnels of these materials. When tunnel sites of

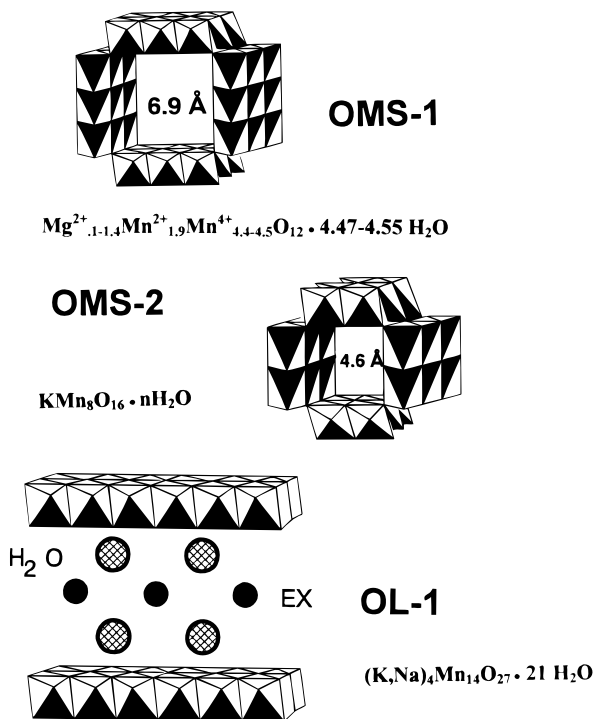


Figure 1. Structure and composition of OMS-1, OMS-2, and OL-1 materials.

OMS-2 materials contain K⁺, the resultant structure type is like the mineral cryptomelane. When Ba²⁺ cations occupy tunnel sites, the structure is similar to the mineral hollandite. Layered manganese oxides (OL-1) have also been prepared which have an interlayer spacing of about 7 Å that contains exchangeable cations and water between the layers.⁶ These materials have structures similar to the mineral birnessite.

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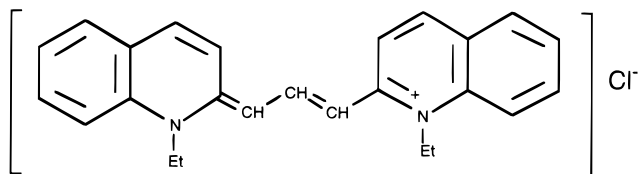


Figure 2. Structure of pinacyanol chloride dye.

Amorphous manganese oxides (AMO) have been prepared by reduction of KMnO_4 with oxalic acid. This material has been found to be an excellent photocatalyst for the conversion of alcohols to ketones and the photodegradation of CH_3Br .⁶ Other catalytic applications of OMS and OL materials involve total oxidation of CO , decomposition of H_2O_2 , dehydrogenation of C_6H_{14} , C_6H_{14} oxidation, 1- C_4H_8 isomerization, and methane oxidation.⁶

This paper reports on the use of OMS, OL, and AMO materials to decompose the cyanine dye, pinacyanol chloride. Pinacyanol chloride (PC) is a cationic, basic dye whose structure is shown in Figure 2. Simple ultraviolet-visible (UV-vis) spectroscopic experiments are used to monitor the amount of dye decomposition, and investigations into dye decomposing kinetics have been made. The effect of H_2O_2 on dye decomposition has been studied. In addition, parameters such as catalyst concentration, pH, and structural changes that occur in the catalysts are examined.

II. Experimental Section

(A) Synthesis of Catalytic Materials. The syntheses of OMS-2 materials doped with Cu, Cr, Co, Ni, and Fe were prepared by refluxing mixtures of KMnO_4 , MnSO_4 , concentrated HNO_3 , and corresponding metal nitrates in aqueous solution for 24 h.³ The metal-doped OMS-2 materials are designated as M-OMS-2. Undoped OMS-2 is referred to as K-OMS-2.

OMS-1 materials were prepared using a precipitation method by reacting NaOH with a solution of MgCl_2 and MnCl_2 and then adding the mixture to a solution of KMnO_4 . A detailed description of this synthesis has been described elsewhere;⁴ however, this method employed KMnO_4 rather than MgMnO_4 in the synthesis. Metal dopants were added as the nitrate salts of Cu^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , and Fe^{3+} .

Layered manganese oxides having the birnessite structure (OL-1) were prepared according to literature procedures.⁶ AMO was prepared by mixing aqueous solutions of KMnO_4 with oxalic acid. A typical synthesis involves reacting a solution containing 1.58 g of KMnO_4 in 100 mL of distilled deionized water (DDW) with 2.26 g of oxalic acid in 100 mL of DDW. The resulting black precipitate was filtered and washed with DDW. Commercial MnO_2 having the pyrolusite structure was provided by Johnson Matthey, Inc., Seabrook, NH.

B. Materials. Pinacyanol chloride was purchased from Aldrich, Milwaukee, WI, and was used without any further purification. PC exhibits a maximum absorbance (λ_{max}) at 544 nm and is purple in neutral and basic aqueous media. Hydrogen peroxide (30%) was obtained from the J. T. Baker Co, Phillipsburg, NJ. Dye and peroxide solutions were made up using distilled deionized water and were prepared fresh daily.

C. Method. Experiments were carried out at room temperature in an open batch reactor by mixing 50 mL

Table 1. Comparison of the Dye-Decomposing Activities of Various Manganese Oxide Catalysts with H_2O_2 ^a

catalyst	% dec ₃₀ ^b
none	0
commercial MnO_2	<1
OL-1	13.3
AMO	45.9
K-OMS-2	50.0
Fe-OMS-2	67.7
Co-OMS-2	51.4
Cu-OMS-2	31.9
Ni-OMS-2	39.5
Cr-OMS-2	58.6
OMS-1	13.3
Fe-OMS-1	17.6
Co-OMS-1	18.1
Cu-OMS-1	9.4
Ni-OMS-1	10.4
Cr-OMS-2	16.5

^a Reaction conditions: 50 mL of 80 ppm PC dye, 50 mL of 1×10^{-3} M H_2O_2 , 25 mg of catalyst, pH = 10. ^b Percent decrease in [PC] after 30 min of reaction.

of each of dye and peroxide and then adding 25 mg of the catalyst. Typical reactant concentrations were 1×10^{-3} M in H_2O_2 and 80 ppm (2×10^{-4} M) in the dye. Reactions were also done in the absence of peroxide by substituting DDW for H_2O_2 . The pH values of the mixtures were adjusted between 6 and 11 by addition of carbonate, borate, and phosphate buffers. The mixture was then allowed to react for 30 min with continuous stirring.

UV-vis measurements were made using a Hewlett-Packard 8452A diode array spectrophotometer. Measurements were taken by removing small aliquots of the mixture (≈ 0.3 – 0.6 mL) at various time intervals during the reaction. The samples were passed through Millipore 0.5 μm syringe filters (Sigma, St. Louis, MO) to remove any solid particulates which tend to scatter the incident beam. The samples were then put into quartz UV-vis cells (path length = 0.2 cm), and the absorbance spectra were measured. Calibration curves for the dye were made by measuring the λ_{max} for a series of standards. Adherence to Beer's law was observed, and linear calibration curves were obtained.

D. Catalyst Structure Determination. Structural data on the catalytic materials were obtained using X-ray diffraction analysis. Measurements were made using a Scintag model PDS-2000 $\theta\theta$ diffractometer. These experiments were performed to see if any structural changes occurred during the reaction.

III. Results

A. Comparison of Catalysts. A systematic comparison of the ability of the various catalysts to decompose the dye in the presence of peroxide was made. These results are given in Table 1. The activity of the catalysts are expressed as the percent decrease in dye concentration that occurs after 30 min. This quantity is proportional to the color loss of the dye during the reactions.

In the absence of any catalyst (1×10^{-3} M H_2O_2 and 80 ppm dye), no dye decomposition is observed after 30 min of reaction. When manganese oxide catalysts are added to the mixture there is a large increase in the rate of decomposition of PC dye. OMS-2 materials show the highest activity (39–65%) followed by AMO (46%). OMS-1 and OL-1 materials show little activity (<20%)

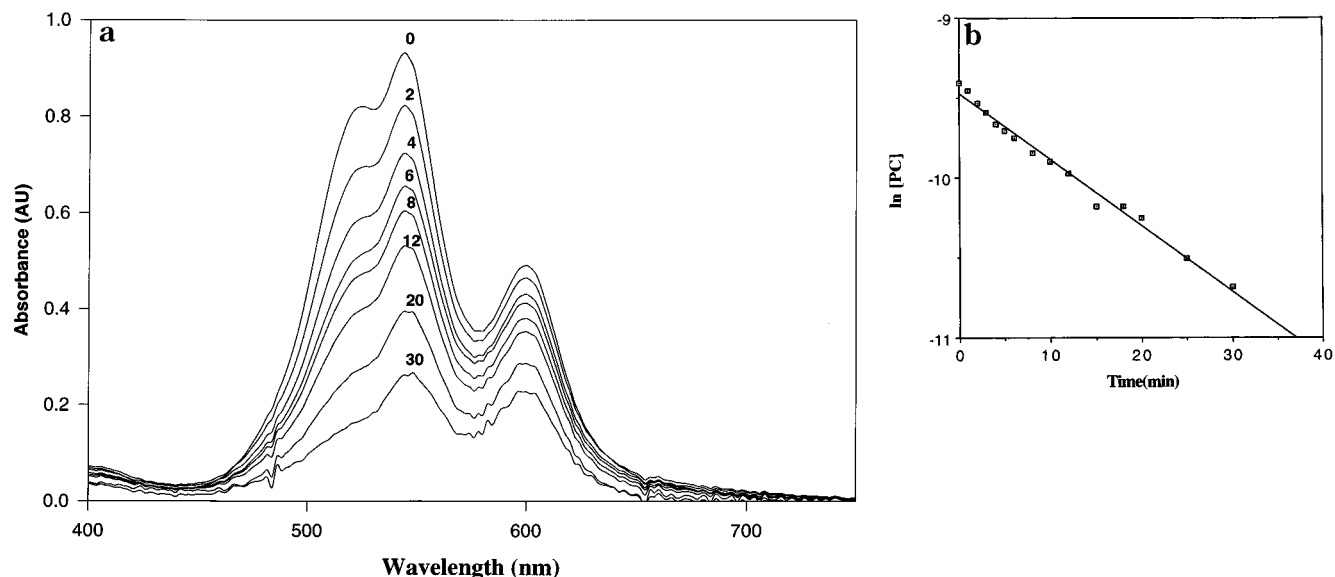


Figure 3. (a) Changes in the visible absorbance spectra of PC dye using K-OMS-2 with H_2O_2 . Time = 0, 2, 4, 6, 8, 12, 20, and 30 min. Conditions: 50 mL of 80 ppm PC dye, 50 mL of 1.0×10^{-3} M H_2O_2 , 25 mg of K-OMS-2, pH = 10. (b) First-order kinetic plot of $\ln [\text{PC}]$ vs time using K-OMS-2 and hydrogen peroxide.

while the commercial MnO_2 (pyrolusite) shows hardly any activity (<1%). The results indicate that addition of dopant metals cause changes in the catalysts' ability to decompose the dye. Because OMS-2 materials showed the highest activity, further in depth studies were carried out by focusing on these materials as catalysts.

B. Kinetic Studies. Kinetic data were collected by taking multiple UV-vis measurements during the course of the 30 min reaction. Figure 3a shows the changes that occur in the UV-vis absorption spectra during a typical reaction using K-OMS-2 as the catalyst. These data clearly show how the dye is decomposed as a function of time. An assumption of first-order kinetics was made and a plot of the $\ln [\text{PC}]$ vs time is shown in Figure 3b. Good linear correlation ($R^2 = 0.988$) is observed suggesting that the reaction is first-order with respect to the dye. The slope of the line reveals a first-order rate constant, $k = -4.1 \times 10^{-2} \text{ min}^{-1}$. These data were also fit to higher order kinetics (i.e., second and third), which resulted in poorer correlation (lower R^2 values).

C. Effect of H_2O_2 . The role of hydrogen peroxide was examined by varying the initial $[\text{H}_2\text{O}_2]_0$ during the reactions. Blank reactions were first done in the absence of any catalysts. PC showed almost no degradation after 30 min at $[\text{H}_2\text{O}_2]_0 < 1 \times 10^{-2}$ M. These reactions were done at room temperature. It is widely known that the bleaching ability of H_2O_2 can be enhanced by increasing the temperature.⁷ To examine this effect, blank experiments were done at higher temperatures. When using $[\text{H}_2\text{O}_2]_0 = 1 \times 10^{-2}$ M at 60 °C, there was a 23% higher reduction in dye concentration compared with similar reactions done at room temperature.

Experiments were then done by varying the initial $[\text{H}_2\text{O}_2]$ with catalysts present. Figure 4 shows the results of such experiments. As the initial hydrogen peroxide concentration is increased, there is a decrease in dye-decomposing activity. In experiments where no

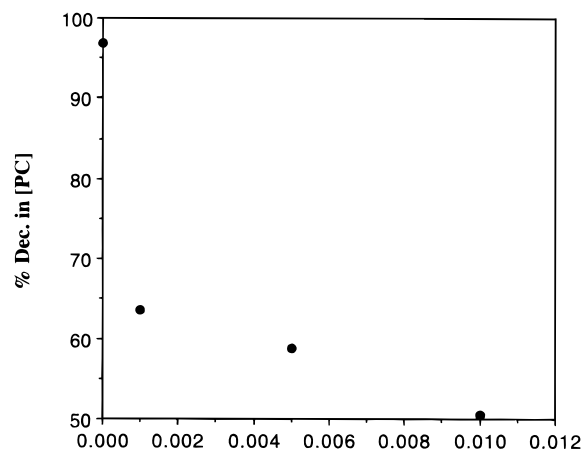


Figure 4. Amount of dye decomposition vs $[\text{H}_2\text{O}_2]_0$ using K-OMS-2. Conditions: 50 mL of 80 ppm PC dye, 50 mL of DDW or 1×10^{-3} , 5×10^{-3} , 1×10^{-2} M H_2O_2 and 25 mg of K-OMS-2, pH = 10. Reaction time = 30 min.

H_2O_2 was used, the concentration of dye was reduced by nearly 100%, and complete decolorization was observed after 30 min. This suggests that peroxide inhibits the dye-decomposing ability of the manganese oxide materials. Therefore, kinetic studies were also done in the absence of peroxide.

Figure 5a shows the changes that occur in the UV-vis absorbance spectra over time using K-OMS-2 as the catalyst with no peroxide. These results show that only 15 min are necessary for complete dye decolorization to occur. Therefore, the rate of the reaction is increased in the absence of peroxide. Figure 5b shows a plot of $\ln [\text{PC}]$ vs time and again shows adherence to first-order kinetics with respect to the dye. The rate constant for this reaction reveals a value of $k = -0.14 \text{ min}^{-1}$, which is 1 order of magnitude higher than the constant for the reaction when 1×10^{-3} M H_2O_2 was used.

D. pH Effects. The effects of pH on the dye-decomposing ability of these systems were examined. Blank reactions using just peroxide and dye showed no dye decomposition after 30 min at pH values of between 8 and 11. There were, however, slight shifts in the λ_{max}

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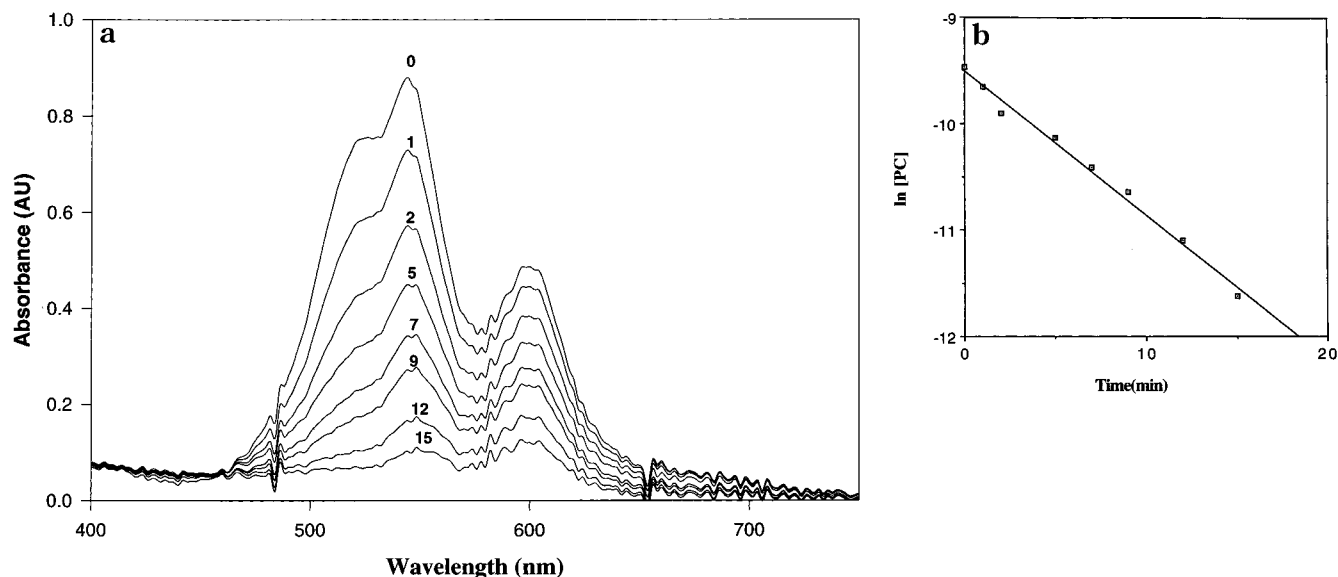


Figure 5. (a) Changes in the visible absorbance spectra of PC dye using K-OMS-2 with no peroxide. Time = 0, 1, 2, 5, 7, 9, 12, and 15 min. (b) First-order kinetic plot of $\ln [PC]$ vs time using K-OMS-2 and no peroxide.

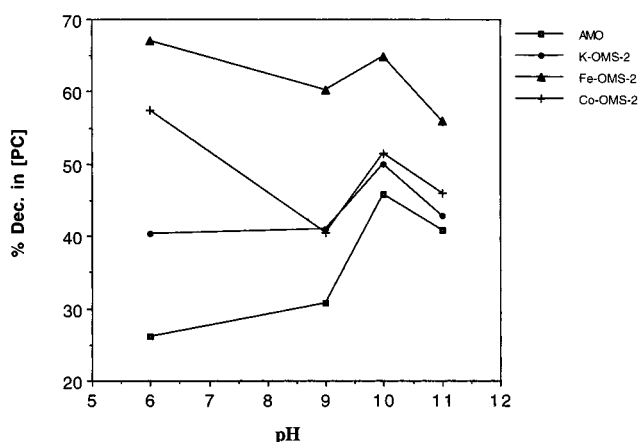


Figure 6. Percent decrease in [PC] vs pH. Conditions: 50 mL of 80 ppm PC dye, 50 mL of 1×10^{-3} M H_2O_2 , 25 mg of catalyst. Reaction time = 30 min. Lines have been added to aid the eye.

of the dye at higher pH values. The dye-decomposing activity for some OMS-2 catalysts were then compared at different pH values.

The results of these experiments are given in Figure 6 for AMO, K-OMS-2, Co-OMS-2, and Fe-OMS-2 materials. The data for AMO and K-OMS-2 show that there is a slight increase in activity as the pH is increased to 10, followed by a sharp decrease at pH = 11. The metal-doped OMS-2 catalysts show different trends as there is a decrease in activity up to pH = 9, an increase at pH = 10, and then another decrease in activity when the pH is increased to 11. These results show that pH significantly influences the rate of these reactions.

E. Variation of Catalyst Amount. The quantity of dye decomposition that occurred when using different amounts of catalysts was examined. Experiments were done by measuring the amount of dye decomposition occurring when 5, 15, 25, and 35 mg of K-OMS-2 catalysts were used. Results of these experiments are shown in Figure 7. These experiments show how sensitive catalyst concentration can be and suggest a first-order dependence in decomposition of the dye.

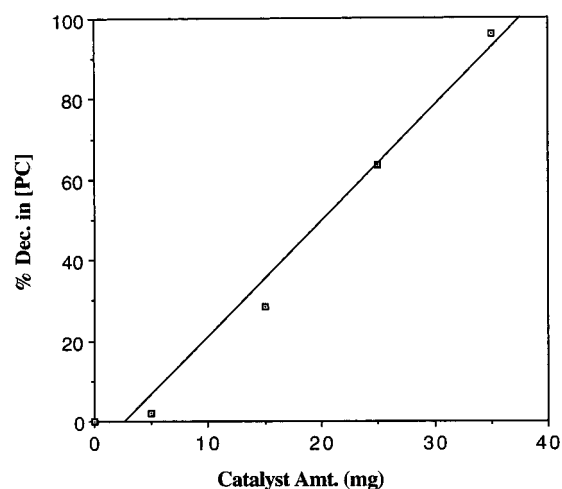


Figure 7. Percent decrease in [PC] vs catalyst amount. Conditions: 50 mL of 80 ppm PC dye, 50 mL of 1×10^{-3} M H_2O_2 , catalyst amount = 0, 5, 15, 25, and 35 mg, pH = 10. Reaction time = 30 min.

F. Structural Changes in the Catalyst. Powder X-ray diffraction measurements were made on K-OMS-2 before and after the reaction to see if any changes in the structure occurred. To recover enough catalyst for these experiments, the reaction was scaled up (200 mL of 1×10^{-2} M H_2O_2 , 200 mL of dye, 100 mg of catalyst). The UV-vis data showed similar kinetics as before. A similar experiment was done using no peroxide. The catalyst was recovered by filtering the reaction mixture after 30 min, and allowing the precipitate to dry in air overnight. X-ray diffraction data were then collected.

The XRD patterns for K-OMS-2 before and after reaction are compared in Figure 8. The XRD pattern for K-OMS-2 before reaction is shown in Figure 8a. Peaks appear at 6.9, 4.9, 3.1, 2.4, 2.2, 1.8, and 1.6 Å, showing good agreement to known K-OMS-2 X-ray diffraction patterns.⁴ The XRD pattern for K-OMS-2 after reaction with peroxide and dye is shown in Figure 8b. The XRD pattern for K-OMS-2 after reaction with no peroxide (DDW) and dye is shown in Figure 8c. The results from Figure 8b,c show that no significant changes occur in the X-ray patterns whether peroxide

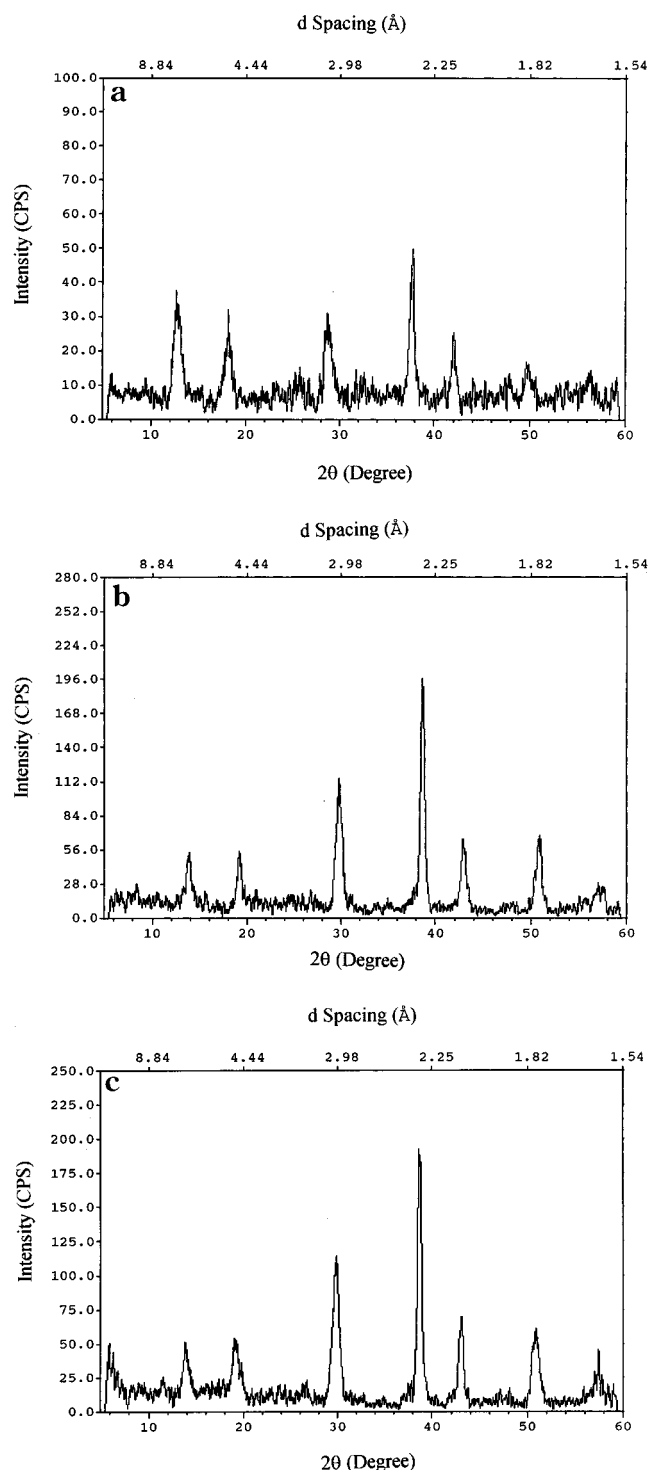


Figure 8. XRD Patterns for K-OMS-2: (a) before reaction, (b) after reaction with dye and H_2O_2 , and (c) after reaction with dye and no H_2O_2 .

is present or not. However, slight shifts in some of the higher d spacing peaks are observed after reaction. For example, comparison of the X-ray patterns of Figure 8a to those of Figure 8b,c show that the peak at 6.9 Å shifts to 6.4 Å while the peak at 4.9 Å shifts to 4.6 Å.

IV. Discussion

Pinacyanol chloride is a soluble organic dye that is stable at $\text{pH} > 4$ in aqueous solutions. Cyanine dyes can be photooxidized,⁷ however experiments showed that no photodegradation of the dye was observed after

30 min. It is likely that pinacyanol chloride is being oxidized by the manganese oxide catalysts. A possible mechanism involves adsorption of the dye molecule on the catalyst surface, electron transfer, and then desorption of the oxidized dye species. If the reaction is allowed to occur for >30 min, a pale yellow color is observed and new peaks are formed in the UV and visible range, suggesting that oxidation may be occurring. Clearly, chemical analyses are needed to determine the nature of the dye degradation products. Unfortunately, the dye is in low concentration and in water which makes such analyses difficult. We are currently exploring techniques such as ion pair reverse phase liquid chromatography for examination of dye degradation products.

Effect of H_2O_2 . Considerable attention has focused on the use of hydrogen peroxide as the active oxidant for several commercial and industrial processes.^{8–12} The destructive oxidation of organic dyes with H_2O_2 has been studied,^{8,10,11} and several species are believed to be responsible for decolorizing colored organic compounds. These include free radical species such as HO^\bullet , HOO^\bullet , or $\text{O}_2^{\bullet-}$.^{8,10} However, the mechanism for dye destruction with H_2O_2 is still in question. A major drawback to the use of H_2O_2 is that its oxidizing strength is decreased at lower temperatures. Therefore, methods of peroxide activation have been developed.^{11,12}

Peroxide activation has been summarized by Strukul¹² and includes (a) reaction of H_2O_2 with Ti(IV), V(V), Mo(VI), and W(VI) (d^0 metal centers) or with Pd(II) and Pt(II) (d^8 metal centers), forming highly reactive metal peroxy and hydroperoxy species; (b) radical decomposition of H_2O_2 with one-electron redox couples such as Fe(II)/Fe(III), known as the Fenton reaction; and (c) use of H_2O_2 as a monooxygen donor to produce highly reactive metal-oxo species. This method has been applied to biomimetic systems using Fe(II), Ru(II), and Mn(II). Several studies have shown that Mn-containing complexes such as manganese polyoxometalate^{13,14} and manganese porphyrins^{15,16} catalyze the epoxidation of alkenes with H_2O_2 . Recently, heterocyclic complexes of Mn were found to selectively oxidize several stains by hydrogen peroxide as well as oxidize polyphenolic compounds.¹⁷ The oxidizing strength of peroxide can also be increased at high pH.^{10,11}

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At room temperature, little or no decolorization of PC was observed after 30 min of reaction using $[\text{H}_2\text{O}_2] \leq 1 \times 10^{-2} \text{ M}$. We anticipated that there might be a positive synergism between hydrogen peroxide activity and manganese oxides. This is not the case and results show that H_2O_2 acts to inhibit the catalysts' ability to decompose PC dye as illustrated in Figure 4. Manganese oxide is known to catalyze the decomposition of hydrogen peroxide to water and oxygen, leading to the partial reduction of manganese(IV) oxide to manganese(III) oxide.^{18–22} Other studies have shown that partial reduction of mixed valent manganese oxides can lead to release of Mn^{2+} into solution.²² Homogeneous decomposition of H_2O_2 by Mn^{2+} can also occur. Therefore, the reaction of H_2O_2 with the catalysts causes deactivation, which leads to less reaction with the dye.

Since these reactions were done under an open atmosphere, the contribution of atmospheric oxygen may be important. Experiments done in the presence of N_2 showed lower activity. However, even in the presence of N_2 , considerable activity was still observed. This is probably due to adsorbed or lattice oxygen being released from the solid. Desorption of oxygen is readily apparent in such systems.^{23,24}

The solubility of manganese oxides is exceedingly small, suggesting that the reaction must be taking place at the interface of the solid and substrate. The XRD data also suggest that no changes in the bulk structure occur after reaction. Since both dye and catalysts contain charged species, electrostatic interactions may be important in the adsorption step. The catalytic activity of manganese oxides may be due to excess surface oxygen rather than active or available oxygen.¹⁸ This may be the case as the XRD data indicate no changes in the catalyst structure.

OMS-2 catalysts show a much higher ability to decompose PC dye than do OMS-1 materials. This may be due to differences in the average manganese oxidation states of these materials. The average manganese oxidation states of OMS-2 and OMS-1 are 3.9³ and 3.6,⁴ respectively. The higher manganese oxidation state of OMS-2 may lead to its greater tendency to decompose PC. This however, does not explain why commercial MnO_2 (pyrolusite) shows almost no activity since it would be expected to have the highest (4+) oxidation state.

Porosity and surface area are important parameters that can control activity. When weighing samples, it was observed that pyrolusite is more dense than OMS and AMO materials. This is in agreement with structural data where pyrolusite would be expected to be less porous and have a smaller surface area than OMS materials due to its 1×1 tunnel structure.²⁵ OMS materials contain 2×2 and 3×3 tunnels and are,

therefore, more porous. Surface areas of all materials range from about $100 \text{ m}^2/\text{g}$ to $250 \text{ m}^2/\text{g}$. In general, higher surface area materials such as AMO and OMS-2 are more active than lower surface area materials such as OMS-1 and pyrolusite. Therefore, surface area and porosity, including the number of surface sites, are likely important in decomposing PC dye.

The addition of dopant metals to OMS-1 and OMS-2 alter the catalytic behavior of these materials. We have shown previously⁶ that electronic, structural, and thermal stability can be changed by adding dopant metals into OMS materials. It is difficult to draw conclusions regarding the effects of dopant metals on decomposing the dye. However, it is clear that both OMS-1 and OMS-2 materials doped with Fe^{3+} , Cr^{3+} , and Co^{2+} show an increase in catalytic activity, while OMS materials doped with Cu^{2+} and Ni^{2+} show less activity than the corresponding undoped materials. These trends are not yet understood. Perhaps the activity is related to the ability to readily form mixed oxidation states, since $\text{Fe}^{2+/3+}$, $\text{Cr}^{2+/3+}$, and $\text{Co}^{2+/3+}$ are more stable than $\text{Cu}^{2+/1+}$ and $\text{Ni}^{2+/1+}$ (or the 3+ states of the latter two species).

Kinetics. The kinetic studies show that in both reactions with and without H_2O_2 first-order kinetics with respect to dye are obeyed. More studies are needed to see if these kinetics are adhered to when different initial dye, peroxide, and catalyst concentrations are varied. Kinetic data may be of interest over various temperatures as well.

The rates of these reactions are clearly affected by pH as seen in Figure 6. The reason for differences in activity with pH is not understood. These experiments were carried out in the presence of $1 \times 10^{-3} \text{ M H}_2\text{O}_2$. It may be necessary to see if these pH trends are similar when done in the absence of peroxide. These data suggest that dopant metals affect the amount of dye-decomposing activity with pH.

The rate of reaction is ultimately controlled by how much catalyst is added to the reaction mixture. The data from Figure 7 show a strong dependency on catalyst amount with dye-decomposing activity. A linear relationship between these two quantities was observed.

V. Conclusions

A relatively simple experimental technique was used to show how several mixed valent manganese oxide catalysts can increase the rate of decomposition of pinacyanol chloride dye. The decomposition of the dye probably proceeds by an adsorption/oxidation/desorption mechanism. Metal-doped OMS-2 materials show the best activities, while OMS-1, OL-1, and commercial MnO_2 show only small increases in the rate of decomposition of PC dye.

Catalysts with dopant metals show variations in their dye-decomposing activities. Fe-, Cr-, and Co-doped OMS materials show enhanced activity compared to that of undoped OMS materials. Ni and Cu dopant metals were found to decrease the activity relative to the activity of undoped materials. The differences in activity among these catalysts are probably due to

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variations in average manganese oxidation states, dopant metal oxidation states, and porosity.

The catalysts were not found to activate H_2O_2 , and its presence appears to inhibit the dye-decomposing activities of the catalysts. Deactivation of the manganese oxide catalysts probably occurs by reduction of the active catalyst surface with H_2O_2 . The rate of decomposition of the dye was greatest when peroxide was absent. Bulk structural data for K-OMS-2 showed that no significant changes occurred after reaction.

In both reactions with and without peroxide, the dye concentration is decreased according to first-order kinetics. Catalyst concentration and pH considerably affect the rate of dye decomposition. More studies are

needed to better understand these trends, especially experiments done in the absence of peroxide. Currently, we are studying whether these catalysts increase the rate of decomposition of several other dye systems.

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