Photochemical Water Oxidation by Zeolite-Supported Manganese Oxides

THESIS

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By

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Abstract

In this work zeolite supported manganese oxide (MnOx-Y(Cl)) clusters were studied for photochemical water oxidation. Zeolite-supported manganese oxides were synthesized by ion exchanging of cations (Mn$^{2+}$ ions with or without alkaline earth metals cations) within zeolite channels and cavities followed by precipitation of manganese oxides on the surface of zeolite. Two types of catalysts were prepared: zeolite-supported manganese oxides (MnOx-Y(Cl)) and zeolite-supported alkaline earth metal cations (N) doped manganese oxides (NMnOx-Y(Cl)). Mn oxides without any support were also prepared. SEM micrographs confirmed the deposition of particles on the zeolite surface with sizes ranging from 50-80 nm. XRD diffraction patterns showed that both MnOx-Y(Cl) and NMnOx-Y(Cl) are hexagonal birnessite type (poorly ordered) layered structure MnO$_2$. Raman scattering also showed that these manganese oxides on the zeolite surface are edge sharing MnO$_6$ octahedra chains, as found in birnessite. XPS characterization showed that all samples had Mn valences as in birnessite. Sacrificial photochemical water oxidation using Ru(bpy)$_3$$^{2+}$-persulfate system showed that zeolite supported catalysts have better catalytic performance compared to non-supported catalysts. It is proposed that the zeolite support provides better dispersion of manganese oxides on its surface, and it brings both photosensitizer and catalysts in close proximity for water oxidation. NMnOx-Y(Cl) were better catalysts than MnOx-Y(Cl) in water oxidation, and we propose that
alkaline earth metals provide structural stability and integrity of the Mn oxide structure and enhances its catalytic activity. Among NMnOx-Y(Cl) catalysts, Ba\(^{2+}\) doped Mn oxides (BaMnOx-Y(Cl)) were the best catalysts, and is correlated with the observation that MnO\(_x\) in BaMnOx-Y(Cl) possess increased surface area exposing more active sites for water oxidation. Overall, alkaline earth metals with the largest cation doped manganese oxides zeolite supported catalysts are found to be the most active water oxidizing catalyst.
Dedication

I would like to dedicate this work to my family. I am grateful to my parents Surendra K. Shrestha and Sandhya Shrestha for always supporting me, believing in me, and guiding me in every step of my life. I dedicate this to my sister Sonu Shrestha, who has always motivated me to do my best. I also dedicate this to all my dear friends who have always stood beside me in the best of times and in the worst of times.
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Chapter 1: Introduction

1.1 Energy crisis

Limited sources of hydrocarbon based fuel energy and increase of greenhouse gases like carbon dioxides by burning fossil fuels such as coal, petroleum, and natural gas are the major environmental issues facing the world\(^1\). At present, burning fossil fuels provides 82% of total energy\(^1\). Extensive and overconsumption of fossil fuel energy has motivated scientists to seek an alternative source of energy that is clean, renewable, and sustainable. In that context, solar energy is an important source of the alternative source of energy. The Sun provides 1.2*10^5 TW of radiation to the earth’s surface, whereas the global consumption rate by comparison was 13.5 TW in 2001\(^2\). The consumption rate is expected to rise to 27 TW by 2050\(^3\). Solar energy is plentiful, and makes natural photosynthesis possible. Natural photosynthesis is an efficient process in nature that involves photo-induced water splitting to provide molecular oxygen (Eq. 1) and also generates glucose through CO\(_2\) reduction (Eq. 2).

\[
2\text{H}_2\text{O} \quad hv \quad \rightarrow \quad \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1)
\]

\[
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad \rightarrow \quad \text{CH}_2\text{O}_{(\text{glucose})} + \text{H}_2\text{O} \quad (2)
\]

\[
4\text{H}_2\text{O} + 4\text{e}^- \quad \rightarrow \quad 4\text{OH}^- + 2\text{H}_2 \quad (3)
\]

Trapping of the solar energy (Eq. 1) and generating hydrogen fuel (Eq. 3) from water splitting is a strategy that scientists have been trying to conceptualize in artificial photosynthetic system using natural photosynthesis as an inspiration\(^4\). Water splitting
comprises of two steps: water oxidation step (Eq. 1) where it involves oxidation of $\text{H}_2\text{O}$ into molecular $\text{O}_2$ and water reduction step (Eq. 3) where generated electrons would be used to generate molecular $\text{H}_2$. This reaction involving water oxidation and reduction is a multi-step and multiple electron process, which would require different redox catalysts. One catalyst facilitates the production of molecular oxygen by oxidizing water, while the other catalyst generates hydrogen by reducing protons. The conversion of solar energy into chemical energy, by generating molecular $\text{O}_2$ and $\text{H}_2$ through water splitting, could contribute to solve global energy crisis. Generating hydrogen gas as a fuel through sunlight driven water-splitting process would be a key step towards achieving renewable energy sources. However, this also necessitates the development of effective materials to efficiently oxidize water, and is one of the biggest challenges in artificial photosynthesis, and thus photolytic water oxidation using water oxidizing catalysts has been an active area of research. The oxidation of water is mechanistically complex as it is not thermodynamically and kinetically feasible ($E^o = 1.23\text{V}$). Being an uphill reaction ($\Delta G^o = 475\text{ kJ/mol}$), the catalytic water splitting reaction is challenging. So scientists are trying to discover catalysts that can oxidize water to give molecular oxygen.

1.2 Natural Photosynthesis

Nature carries out photo induced water oxidation in its photosynthetic process, which is one of the steps in converting solar energy into chemical fuel energy. It involves the trapping of solar energy, inducing charge separation, and ultimately resulting in catalytic water oxidation. Photosystem II (PS II) is a membrane protein complex found in thylakoid membranes. Absorbing solar energy excites the arrays of pigments
(chlorophyll) present in photosynthetic organisms and leads to a series of electron transfer reactions leading to a charge separation state with oxidized PSII reaction centers. Neighboring tyrosine residue (Yz) reduces the oxidized PS II center. And consequently, the oxidized Yz residues are involved in the extraction of four electrons from oxygen evolving complex (OEC) present in the PSII, and ultimately OEC oxidizes two water molecules into molecular oxygen\(^9\text{-}^{11}\). PS I also get excited after entrapping solar energy, and involves in the reduction of NADP\(^+\) to NADP\(^{23}\). The full scheme of natural photosynthesis is shown in Figure 1.

Scientists have determined that the oxygen-evolving center (OEC) of PSII is a calcium manganese oxide cluster. Kamiya group has explored the crystal structure of OEC of PSII of T. vulcanus at a resolution of 1.9\(\text{Å}\). It consists of a \(\text{Mn}_4\text{CaO}_5\) cluster with a cubane like structure (as shown in Figure 2)\(^{11}\). The manganese atoms are bonded with the aid of \(\mu\text{-oxo}\) bridges. The fourth Mn and O are found outside of cubane structure forming a distorted chair structure surrounded by a protein envelope. \(\text{Ca}^{2+}\) ion is tightly bound to the Mn active center and suggested to be an integral part for water oxidation\(^9,^{10,^{12,13}}\). Through Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) studies done by Yachandra group, it is postulated that \(\text{Ca}^{2+}\) is closely associated with Mn active center in OEC\(^{13}\).

In OEC cluster, Mn acts as the active metal site for the water oxidation that undergoes different \(S_n\)-transition states in which each \(S_n\) state refers to oxidation state of Mn cluster (Kok Cycle)\(^{11}\). Two water molecules are ligated to both calcium and manganese\(^9\). It has been proposed that by proton coupled electron transfer (PCET)
mechanism, oxidized Yz residue extracts proton from MnIV-OH which results in an
electron-deficient MnV=O (S4 state)9,10,14. Ca2+ provides not only the structural stability to
the OEC cluster but also plays a functional role in water oxidation. The ligated water on
Ca2+ loses its proton to neighboring protein residue B and the resulting hyroxide does a
nucleophilic attack on MnV=O resulting in O-O bond formation 9,10. Removal of Ca2+
from OEC of PSII interferes with S2 transition state, as a result of which water splitting is
halted14. Even though there are many proposed mechanisms elucidating the function of
Ca in the WOC of OEC in PSII, this problem is still unresolved. Studies have focused on
the effect of substituting Ca2+ by other alkaline earth metal cations such as Sr2+ and alkali
metal cations Li+, Na+, K+, Rb+, and Cs+ 15,16,17. Shen group studied Sr- substituted PSII
and reported decrease in catalytic activity of OEC, even though it is the only metal ion
that can substitute Ca2+ and give some catalytic activity of PSII 9,16,18. This implied that
Sr2+ ion, which has comparable size and Lewis acidity to Ca2+ ion, was not able to
perform as efficiently as Ca2+ ion in OEC cluster. Alkali metal ion substitution inhibited
the catalytic activity of PSII significantly, which suggests that ionic radius of the cation
occupying Ca2+ binding site is also crucial15.

Along with manganese and Ca2+, Cl− is also a constituent of OEC which is
suggested to act as a cofactor to stabilize the redox potential of Mn19. Brudvig group
proposed that Cl− is ligated to both Ca2+ and Mn such that after the formation of MnV=O
moiety, Ca-Cl bond elongates whereas MnV-Cl bond contracts10. The elongation of Ca-Cl
bond increases the Lewis acidity of Ca2+, consequently promoting the nucleophilicity of
Ca-ligated water. Depletion of Cl− in OEC is also suggested to inhibit the S-transition

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cycle\textsuperscript{10,20}. These studies have shown that Cl\textsuperscript{-} is required for electron transfer between manganese ions within the oxygen-evolving complex\textsuperscript{20}. Studies of substitution of Cl\textsuperscript{-} of OEC in PSII by different anions such as Br\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, I\textsuperscript{-} has been reported, and the conclusion is that the Cl\textsuperscript{-} ion is an indispensible factor in PSII water oxidation mechanism\textsuperscript{18,20,21,22}. The WOC of PSII is an extremely efficient catalyst that can catalyze water oxidation into oxygen and proton in neutral pH conditions and low over potential condition (~160 mV) with turn over frequency (TOF) of 25\texttimes10\textsuperscript{3} mmol\textsubscript{O\textsubscript{2}}mol\textsuperscript{-1}Mn\textsuperscript{-1} (per Mn active center)\textsuperscript{11}.

1.3 Artificial Photosynthesis:

Adopting the natural photosynthesis scheme as a role model, scientists have explored artificial photosynthesis systems for generation of solar fuels and other chemicals through different nanostructured materials\textsuperscript{1,23}. Nature can produce oxygen from water, but it is difficult to achieve the same redox reaction synthetically\textsuperscript{4,5}. There are several reported metal complexes that act as light harvesting centers and induce charge separation for the water oxidation catalysis, and catalysts for water oxidation. Like in nature, there are requirement of specific photosensitizers, electron mediators, and catalytic metal clusters that can harvest solar light, induce charge separation, and finally oxidize water to give molecular oxygen and release of protons\textsuperscript{5}.

Different photosensitizers have been explored including porphyrins that trap the light via $\pi-\pi^*$ transition. From nanotube to nanoantenna arrays, from light harvesting inorganic to organic dendrimers, from metal coordinated to non-metal complexes, there have been studies for visible light absorbing harvesting structures. Ruthenium complexes
such as 2,2’-trisbipyridyl ruthenium [Ru(bpy)$_3^{2+}$] and its derivatives are well known photosensitizer and one-electron oxidant which can oxidize water to oxygen on the surface of heterogeneous catalysts$^{24}$.

The overall scheme of photocatalytic water oxidation of water by Ru(bpy)$_3^{2+}$-catalyst is shown in Figure 3. Steps that involves the photochemical water oxidation in the Ru(bpy)$_3^{2+}$-persulfate system are shown below. The step 1 shows the trapping of the visible light (absorption peak at 450 nm) through metal to ligand charge transfer (MCLT) from d-orbitals of Ru$^{2+}$ to the $\pi^*$ orbitals to the conjugated bipyridyl ligands$^{25,26}$. The excited from triplet state Ru(bpy)$_3^{2+*}$ is long-lived and can be oxidized by sacrificial acceptor as shown in step 2$^{27}$. The reduction potential of redox pair [Ru(bpy)$_3^{2+}$/[Ru(bpy)$_3^{3+}$] is 1.24 V vs. NHE. The sacrificial electron acceptors such as peroxodisulfate (Na$_2$S$_2$O$_8$) (step 2) or cobalt (III) pentammine chloride [Co(NH$_3$)$_5$Cl]$^{2+}$ (step 4) can react with photoexcited state of photosensitizer (Ru(bpy)$_3^{2+*}$) and undergoes irreversible reduction reaction to form Ru(bpy)$_3^{3+}$ (step 2). These sacrificial acceptors have been reported in several experimental studies. The oxidized Ru(bpy)$_3^{3+}$ photosensitizer donates its hole to the water oxidizing catalysts, and at that site water oxidation take places as shown in step 3 below. The step 3 is the water oxidation step for which effective catalysts are being investigated. This reaction usually proceeds in mildly acidic conditions$^{25}$. In the absence of homogeneous or heterogeneous water oxidizing catalysts, Ru(bpy)$_3^{3+}$ undergo fast decomposition as it forms a Ru(bpy)$_3$:OH$^{2+}$ product$^{25}$. 
Ruthenium complex oxidation using sodium persulfate

\[ \text{Ru(bpy)}_3^{2+} \xrightarrow{hv} \text{Ru(bpy)}_3^{2+*} \quad (1) \]

\[ 4\text{Ru(bpy)}_3^{2+*} + 2\text{S}_2\text{O}_8^{2-} \rightarrow 4\text{Ru(bpy)}_3^{3+} + 4\text{SO}_4^{2-} \quad (2) \]

\[ 4\text{Ru(bpy)}_3^{3+} + 2\text{H}_2\text{O} \xrightarrow{\text{WOC}} 4\text{Ru(bpy)}_3^{2+} + 4\text{H}^+ + \text{O}_2 \quad (3) \]

Ruthenium complex oxidation using \([\text{Co(NH}_3)_5\text{Cl}]^{2+}\)

\[ \text{Ru(bpy)}_3^{2+*} + [\text{Co(NH}_3)_5\text{Cl}]^{2+} \xrightarrow{hv} \text{Ru}^{\text{III}}(\text{bpy})_3^{3+} + \text{Co}^{2+} + 5\text{NH}_3 + \text{Cl}^- \quad (4) \]

1.4 Homogeneous and Heterogeneous Catalysts:

Several homogeneous and heterogeneous catalysts have been explored for the water splitting reactions. Bio-inspired heterogeneous compounds and nanostructures, homogeneous molecular complexes, and nanobiocatalytic assemblies have been explored in order to enhance the water oxidation in artificial photosynthesis system\(^5,23,28,29,30,31,32\). Homogeneous and heterogeneous catalysts have their own merits and demerits on the basis of its stability, mechanism clarity, and robustness. The catalytic mechanism studies of homogeneous catalyst are understandable in terms of elucidating the intermediates involved in mechanistic pathway; however they usually have stability issues. In natural photosynthesis, the WOC in OEC of PSII is a bio-homogeneous catalyst, which is both very efficient in removal of four electrons and four protons from the catalytic site, but it has always remained a challenge to synthesis a homogeneous catalyst that is stable and robust\(^32\).

Meyer and his co-workers have developed a molecular dinuclear ruthenium based WOC known as blue dimer, a ruthenium complex \([(\text{bpy})_2(\text{H}_2\text{O})\text{RuORu(}\text{H}_2\text{O})-(\text{bpy})_2]^{4+}\).
which in the presence of excess \((\text{NH}_4)_2[\text{Ce}^{IV}(\text{NO}_3)_6]\) (Cerium Ammonium Nitrate: CAN) has turnover numbers (TON) of 13.2 towards water oxidation\(^{33}\). They studied the mechanistic pathway for oxygen evolution thoroughly and proposed that an oxido species of Ru at the highest oxidation state is attacked by water molecule producing a hydroperoxide species, which is oxidized intermolecularly by the Ru\(^V=O\) to release molecular oxygen\(^{34}\). Ammine-coordinated Ru complexes in homogeneous aqueous solution also have been studied such as \([\text{(NH}_3)_5\text{Ru}^{III}(\text{μ}-\text{O})\text{Ru}^{IV}\text{(NH}_3)_4(\text{μ-O})\text{Ru}^{III}\text{(NH}_3)_5]^{6+}\) with CAN with turnover number of 75\(^{35}\). The first mononuclear Ru complexes “2,6-bisnaphthridyl-4-tertbutylpyridine” have also been reported for photocatalytic water oxidation with turnover number 580\(^{36}\). The problem with the organic ligands is that they tend to participate during water oxidation reaction, which implies degradation of the catalyst\(^{37}\). To improve the robustness of the catalyst, all inorganic system such as polyoxometalate (POM) have been reported\(^{38}\). Ruthenium POM complex have been reported by Geletii et al. to be an efficient water oxidizing catalyst with turnover number of 23 per active center\(^{39}\). Adopting same strategy, Yin et al. was successful in synthesizing a Co-POM complex comprising Co\(_4\)O\(_4\) core with very high catalytic rate of visible light driven water oxidation by \([\text{Ru(bpy)}_3]^{3+}\) at pH 8.0\(^{40}\). Colloidal IrO\(_2\) has been reported for photolytic water oxidation\(^{25}\). There are homogeneous complexes that act as precursors to heterogeneous water oxidizing catalyst. Organometallic iridium complexes such as \([\text{Cp}*\text{Ir(H}_2\text{O})_3]^{2+}\) has been reported by Brudvig and his coworkers as a precursor to form an active iridium oxide heterogeneous water oxidizing catalyst upon electrochemical oxidation on the anode\(^{41-43}\). Silica-supported
[Ru(bpy)_3]^{2+} polymeric sensitizers and colloidal IrO_2 system has also been reported to oxidize water buffered at mildly acidic range of silicate buffer\(^{44}\). Even though they show high catalytic activity for water oxidation, Ru and Ir complexes as precursors or catalysts are not practical. These noble elements are expensive and rare. Thus scientists have explored other elements such as manganese, cobalt, nickel and iron complexes as water oxidizing catalysts.

Limburg and Brudvig suggested that di-μ-oxo Mn\(^{III}\)Mn\(^{IV}\) binuclear complexes with planar tridentate ligands can provide the site for water oxidation\(^ {45} \). There is a report of \(((tpy)(H_2O)Mn^{III}(μ-O)_2Mn^{IV}(tpy)(H_2O))^3^+ (tpy = 2,2’-6’,2”-terpyridine)\) complex as water oxidizing catalyst after reaction with hypochlorite, reporting TON of 4 but with decomposition of the complex\(^ {46} \). They also showed that oxygen was evolved from water, and not from oxidant through O\(^{18}\) isotope-labeling experiment. The dinuclear Mn complex, \([Mn_2(OAc)_2(bpmp)]^+ (bpmp= 2,6-bis[[N,N-di(2-pyridylmethyl)amino]methyl]-4-methyl-phenol)\) has been reported for water oxidation catalysis in oxone, but also results in CO\(_2\) gas evolution due to ligand oxidation\(^ {47} \). Naruta et al. proposed covalently linked manganese porphyrin dimers for water oxidation in homogeneous system\(^ {48} \). There are several other molecular complexes of Mn, e.g. tetramanganese complex \([L_6Mn_4O_4]\) (L=diphenylphosphinate) with a Mn\(_4\)O\(_4\) core releasing O\(_2\) molecule from cubane core\(^ {49} \).

Since homogeneous complexes have stability issues, scientists are looking for heterogeneous catalysts, which demonstrate more robustness in catalytic activity compared to homogeneous catalysts are being explored. Even though the mechanistic
study for heterogeneous catalytic activity is more difficult, its practical application has a significant merit for water oxidation. Usually heterogeneous catalysts are metal oxides and hydroxides of Fe$^{III}$, Co$^{II,III}$, Mn$^{III,IV}$.

Nocera group reported electrochemical deposition of cobalt phosphate (CoPi) on ITO (Indium Tin Oxide) for water oxidation catalysis at neutral pH and ambient condition$^{50}$. Fukuzumi group showed metal doped cobalt oxides such as LaCoO$_3$ can act as an robust and efficient catalyst in visible light driven water oxidation in presence of persulfate and photosensitizer [Ru(bpy)$_3$]$^{2+}$ with O$_2$ yield of 76%$^{51}$. It has been shown that nanostructured spinline Co$_3$O$_4$ clusters are water-oxidizing catalysts$^{51}$. Similarly NiFe$_2$O$_4$ is also reported as a visible light driven water oxidizing catalyst with 74% O$_2$ yield with high reusability$^{52}$.

Manganese oxides also have the potential as water oxidation catalysts. Manganese is an earth abundant element, economical, and found in OEC in PSII. Harriman et al. reported that colloidal MnO$_2$ exhibits slow catalytic performance of water oxidation$^{53}$. Jiao group introduced nanostructured manganese oxides such as α-MnO$_2$ nanotubes, α-MnO$_2$ nanowires, and β-MnO$_2$ nanotubes as highly efficient and robust catalysts in Ru(bpy)$_3$]$^{2+}$-S$_2$O$_8^{2-}$ system$^{54}$. They reported that crystal structure or morphology of the catalysts does not influence the photocatalytic activity. Amorphous manganese oxides (AMO), octahedral molecular sieves (OMS-2), and octahedral layered manganese oxides (OL-1) manganese oxides have been reported to be water oxidizing catalyst using both CAN and Ru(bpy)$_3$]$^{2+}$-S$_2$O$_8^{2-}$ system by Suib and Dutta group$^{55}$. AMO showed the highest TOF (mmol$_{O_2}$/mol$_{Mn}$ s$^{-1}$) of 0.52 and 0.046 of dissolved oxygen evolution kinetics in
presence of CAN and Ru(bpy)$_3^{2+}$-S$_2$O$_8$ system (measured with Clark electrode) respectively. AMO also showed high dissolved oxygen evolution with high reusability measured by Gas Chromatography (GC). Nakamura group showed layered δ-MnO$_2$ as efficient electrocatalysts for water oxidation in strongly alkaline condition$^{56}$. They demonstrated that Mn$^{3+}$ accumulation in MnO$_2$ layers at high pH is the main active electrocatalysts for water oxidation with a small overpotential in the wide range of pH (4-13). Dismukes group studied crystalline polymorphs of manganese oxides such as α-MnO$_2$, β-MnO$_2$, λ-MnO$_2$, Mn$_3$O$_4$, Mn$_2$O$_3$, and LiMn$_2$O$_4$, and mentioned that Mn$^{III}$-O weaker and flexible bonds participate in the water oxidation actively and also Mn based catalysts are degraded due to disproportion of Mn$^{III}$ into Mn$^{II}$ and Mn$^{IV}$ oxidation states$^{57}$. LiMn$_2$O$_4$ acts as efficient water oxidizing catalyst after delithiation of lithium resulting in cubane Mn$_4$O$_4$ cores in the Ru(bpy)$_3^{2+}$-S$_2$O$_8^{2-}$ system in mildly acidic condition$^{58}$. There has been report of Ni-doped Mn oxide catalyst as NiMnO$_3$ in the visible light-driven ([Ru(bpy)$_3^{2+}$-S$_2$O$_8^{2-}$ system) and electrochemical water oxidation$^{59}$. The NiMnO$_3$ showed high catalytic activity compared to other manganese oxides like α-MnO$_2$, Mn$_2$O$_3$, and Mn$_3$O$_4$. Dau group also demonstrated that electrodeposited amorphous Mn oxide containing Mn$^{III}$ has higher catalytic activity because of disorder in the atomic lattice structure of MnO$_6$ octahedra$^{60}$. Nam group has studied a new pyrophostate based Mn compound (Li$_2$MnP$_2$O$_7$) as a new water oxidation catalyst and also reported that high Mn$^{III}$ content in the catalyst enhances the catalytic activity$^{61}$.

Frei group reported that the nanosized manganese oxide clusters supported on mesoporous silica (KIT-6) are an efficient visible light driven oxygen evolving catalyst at
mildly acidic conditions. They suggested that silica support provides high surface area for dispersion of the catalyst on the surface, and retains the active Mn centers of the catalyst by assisting in deprotonation during photocatalysis, consequently reducing pH around active Mn centers and ultimately preventing Mn from leaching. Najafpour et al. have extensively studied the nanoscale Mn oxides as a water oxidizing catalyst and this group studied $\alpha$-Mn$_2$O$_3$ in the presence of CAN as a non-oxo transfer oxidant and reported to have 0.15 TOF. They showed that higher concentration of CAN depresses the oxygen evolution capability of the catalysts.

Doping Ca$^{2+}$ ions in manganese oxides has been proved to improve the catalytic activity as observed in OEC. Inspired from the natural photosynthesis OEC (Mn$_4$CaO$_5$ cluster), Najafpour group has also studied calcium manganese oxides. The catalyst was synthesized by treating calcium nitrate and manganese chloride in presence of potassium permanganate in highly alkaline condition followed by calcination. The oxygen evolution kinetics of CaMn$_2$O$_4$.H$_2$O was measured with both CAN and $[\text{Ru(bpy)}_3]^{2+}/[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ system with TOF of 0.540 and 0.350, respectively. The oxygen evolution was studied in the presence of other oxidants such as peroxides and HSO$_5^-$. They proposed that the role of calcium in their catalyst is similar to PSII-protoenzyme. They also synthesized nano-sized CaMn$_2$O$_4$.H$_2$O and found of TOF 2.0 in presence of CAN. Due to nano-size of the catalyst, the performance is enhanced significantly. They have also synthesized calcium manganese based water oxidizing catalysts CaMnO$_3$, Ca$_2$Mn$_3$O$_8$, CaMn$_4$O$_8$, and CaMn$_3$O$_6$ and tested in presence of CAN.
Dau group has synthesized manganese calcium oxide\textsuperscript{69}. They found that those active catalysts CaMn\textsubscript{2}O\textsubscript{4}.H\textsubscript{2}O and CaMn\textsubscript{2}O\textsubscript{4}.4H\textsubscript{2}O have disordered interconnected MnO\textsubscript{6} octahedra identified by X-ray Absorption spectroscopy (XAS). They proposed that these catalysts are the closest analogs of PSII complex considering three common features, such as Mn with oxidation potential between +3 and +4, disorderly structured Mn oxide layers with unsaturated $\mu_2$-OH bridges between Mn ions, and lastly presence of $\mu$-oxido bridging of Ca to Mn ions. Kurz group also studied calcium birnessite as water oxidation catalysts in presence of CAN. They figured the optimal synthesis parameters such as Ca:Mn ratio and temperature, however provided no insight about the nature of active sites concerning O-O bond formation\textsuperscript{70}. Kurz group also studied layered manganese oxides birnessites for water oxidation based on different alkaline earth metals, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, and Mg\textsuperscript{2+} ions (as shown in Figure 4)\textsuperscript{71}. For birnessites, the following order of catalytic activity: Ca\textsuperscript{2+}$>$ Sr\textsuperscript{2+} $>>$ Mg\textsuperscript{2+}~ Na\textsuperscript{+} in presence of CAN is observed. The highest TOF of oxygen evolution was that of Ca-birnessite with 0.40. They proposed that since the structure of Ca-birnessite matched the structural motif of OEC of PSII, the role of Ca\textsuperscript{2+} should be similar to OEC as active site for terminal or bridging oxygen atoms for O-O bond formation.

Najafpour et al. have reported that nano-sized manganese oxides (0.7-2.0 nm in size) on faujasite zeolite showed water oxidizing activity in the presence of CAN (0.05-0.50 M) with TOF of 2.62\textsuperscript{72}. However, zeolite structure gets destroyed in such high acidic condition. Their reported X-ray Diffraction pattern of zeolite seemed to show destruction of crystalline faces of zeolite. The issue with CAN is that this primary water oxidant is
stable only in highly acidic range (pH~ 0.8-0.9), which is not applicable to natural photosynthesis, which is in neutral pH range. The reduction potential of Ce$^{4+}$/Ce$^{3+}$ is 1.7 V vs. NHE.

$$4\text{Ce}^{IV} + 2\text{H}_2\text{O} \xrightarrow{\text{WOC}} \text{O}_2 + 4\text{H}^+ + 4\text{Ce}^{III}$$

Slightly above that acidic range, Ce (IV) tends to form insoluble cerium oxides and also incorporates other metals, which complicates the mechanistic studies of water oxidation. Thus its narrow range of pH stability limits its application.$^{73}$

There also has been a report of zeolite supported cobalt (II) hydroxides and oxides for photocatalytic water oxidation$^{74}$. Starting with $\beta$-Co(OH)$_2$ on zeolite surface spinel, Co$_3$O$_4$ was formed due to thermal treatment as a topotactic transformation. They found $\beta$-Co(OH)$_2$ with higher catalytic activity compared to spinel oxides in Ru(bpy)$_3^{2+}$-S$_2$O$_8^{2-}$ system in phosphate buffer. However, the catalytic activity of regenerated catalyst was low compared to fresh catalyst, which means that the catalysts do not exhibit robustness. Most importantly, they have suggested that anchoring of catalyst on zeolite surface provides better stability through immobilization and wide dispersion of catalyst on the surface. The negative charge on the zeolite scaffold also attracts Ru(bpy)$_3^{2+}$ which means the greater accessibility of the oxidant.

1.5 Zeolites:

Zeolite was first discovered in 1756$^{75}$, since then about 140 zeolitic frameworks are known$^{76}$. Zeolites are microporous crystalline aluminosilicates with the pores and cavities of molecular dimensions. It has the framework made up of T-O-T bonds (T= Si,
Al) connecting TO₄ tetrahedra⁷⁶,⁷⁷. The general formula for the zeolite can be represented as:

\[ \text{M}^{+\times/n}[\text{(AlO}_2^-)_x \text{ (SiO}_2)_y] \cdot \text{wH}_2\text{O}^{(77,79)} \]

where \( x \) and \( y \) are the number of tetrahedral atoms per unit cell and \( n \) is the valence of the cation \( \text{M} \). Due to the presence of Al in the zeolitic framework, alumina tetrahedra has a residual negative charge as Al possess 3+ charge. In order to counter balance excess negative charges, additional positive charges are provided from cations \( \text{M} \) (usually alkali and alkaline earth metal cations) introduced in the structure through ion exchange in aqueous solutions⁷⁸. The Si/Al ratio is important for zeolitic framework as it determines the hydrophobicity as well as hydrothermal stability of zeolite. Zeolites have well defined pore structures with a large surface area and tunable surface properties, and range from micrometer to nanometer size. Faujasite (FAU) type zeolite also known as Zeolite Y (ZY) structure if it has Si/Al ranging from 1.5 to 3 (Figure 5)⁷⁹. In this work, commercial zeolite Y was used with Si/Al of 2.55 with Na⁺ ions as a counterbalance. The basic units for ZY are the sodalite cages which are arranged in the three-dimensional array to create the porous cavity called supercages which is about ~12 Å in diameter and the size of opening of 12-membered ring of ZY is 7.4 Å⁷⁷. The S6R units (6-oxygen window) links the sodalite cages in zeolite. The ion-exchanging properties, high surface area, and high thermal stability of zeolite have made them useful for a wide range of applications in agriculture, petroleum cracking, catalysis, and waste water treatment⁷⁶.

Studies have already been done with manganese oxide clusters supported on mesoporous silica, which suggested that mesoporous silica scaffold provide high surface
area for stable dispersion of the nanostructured Mn oxides as well as protecting the Mn centers from deactivation due to surface restructuring. Zeolite framework can also be a potential candidate as inert support for the catalyst, which can preserve its integrity. Ruthenium oxide (RuO$_2$) on zeolite Y has been reported to be efficient water oxidizing heterogeneous catalyst for hydrogen evolution. It has high surface area, which can help in wide dispersion of catalysts on its surface and leads to more exposure of active sites for catalysis. As mentioned earlier, Del-Pilar et al. have suggested that anchoring of catalyst on zeolite surface in better stability through immobilization and better dispersion of catalyst on the surface. The negative charge on the zeolite scaffold also attracts photosensitizer/oxidant Ru(bpy)$_3^{2+}$ which means the catalyst dispersed on the zeolitic surface has greater accessibility of the oxidant, which ultimately enhances the water oxidation in the presence of the catalyst. In case of zeolite-supported catalyst, CAN is not applicable because zeolites are not stable in such high acidic conditions. The leaching of aluminium from the zeolite starts to take place at low pH condition, which causes the degradation of zeolitic framework.

Zeolite has been exploited for investigation of photoelectron transfer within zeolite cage and artificial photosynthesis systems for photolytic water splitting. Photochemically separated electron and holes can be transferred within zeolite cages. Retarding the back electron transfer process in the donor-acceptor system, Ru[(bpy)$_3$]$^{2+}$ and methyl viologen, Dutta group has been able to demonstrate the usage of zeolitic framework for assembly of redox pair in the system. Dutta group has also studied these Ru(bpy)$_3^{2+}$-viologen pair with the catalyst RuO$_2$ on zeolite membrane. This approach is
mimicking the natural photosynthetic process to create the charge separation states. The attached photoactive species like Ru(bpy)$_3^{2+}$ on the zeolite membrane can trap the solar energy, which results in electron transfer between Ru(bpy)$_3^{2+}$ to viologen in the zeolite cage resulting in photochemical charge separation (Figure 6). The close proximity of all species as well as the steric binding of photoactive species into a zeolite supercage slows down the back electron transfer reaction, which induces long-lived charge separation. The electron-hole pair can be separated within zeolite membrane where the catalyst to produce oxygen captures four holes and on the other hand the four electrons are trapped by a separate catalyst on the other side of the membrane like RuO$_2$ to produce hydrogen.

In this work, we study if manganese oxides supported on zeolite can function as efficient water oxidizing agent to produce molecular oxygen. Zeolite-supported manganese oxides are synthesized by ion exchanging of cations (Mn$^{2+}$/alkaline earth metal cations) within zeolite followed by precipitation of manganese oxides on the surface of zeolite. We study its water oxidizing catalytic activity in photochemical Ru(bpy)$_3^{2+}$-persulfate system. If this looks promising then we intend to design the entire artificial photosynthetic model and scheme using zeolite membrane and these catalysts. In broader picture, we are aiming for the separation of water splitting products: molecular oxygen and molecular hydrogen through artificial photosynthesis scheme using zeolite membrane.
Figure 1: Simplified scheme of natural photosynthesis process. [Ref: 23]

Figure 2: Crystal structure of Mn₄CaO₅ cluster at 1.9Å° resolution from Umena et. al. (W: Water) [Ref: 12]
Figure 3: Schematic of the photocatalytic oxidation of water in photochemical Ru[(bpy)$_3$]$^{2+}$- S$_2$O$_8^{2-}$ system [Ref: 25]

Figure 4: Layered structure of manganese oxides (like birnessite) proposed by Wiechen et al. (M= alkaline earth metal cations) [Ref: 72]
Figure 5: Structure of faujasite zeolite (ZY) viewed [111] plane. [Ref: 85]
Figure 6: Artificial photosynthesis system comprising of photoactive species, oxygen and hydrogen evolving catalysts assembled in zeolite membrane [Ref: 84]
Chapter 2: Experimental Section

2.1 Synthesis of water oxidation catalyst

2.1.1 Synthesis of manganese oxide catalyst:

In the volume of 50 mL deionized (DI) water, 2.0 mmol of manganese (II) acetate tetrahydrate (Mn(CH$_3$COO)$_2$.4H$_2$O) and 1 mmol of KMnO$_4$ crystals was stirred for 15 minutes at room temperature (RT). The color of the solution immediately changed from white to black color upon addition of KMnO$_4$. The solution was filtered, washed, and dried in vacuum. Then the dried oxidized sample (MnOx*) was treated with 3.0M KCl of 50 mL solution and stirred for 2 hours at RT followed by washing (~0.7 to 1 L of DI water) and drying in vacuum and the resulting catalyst was MnOx (Cl).

2.1.2 Synthesis of zeolite supported manganese oxide catalyst:

Micron-sized zeolite Na-Y (ZY) with Si/Al ratio of 2.55 was purchased from Zeolyst International. In a 50 mL DI water, 2.0 mmol of Manganese (II) acetate tetrahydrate (Mn(CH$_3$COO)$_2$.4H$_2$O) and 0.5 g of Zeolite Na-Y (ZY) were added and stirred for 24 hours at room temperature (RT). The Mn-ion exchanged (Mn-Y) solid was filtered washed with DI water, dried in vacuum overnight. The Mn-Y powder was treated with 1 mmol of KMnO$_4$ in 50 mL DI water which was stirred for 2 hours at RT followed by filtration, washing, and drying in vacuum. The color of Mn-Y sample changed from white to dark brown color. Then oxidized sample (MnOx-Y*) was treated with 3.0M KCl
of 50 mL solution in order to remove the residual Mn\(^{2+}\) within the zeolites. The solution was stirred for 2 hours at RT followed by washing (~0.7 to 1 L of DI water) and drying in vacuum, and the resulting catalyst was MnOx-Y(Cl).

2.1.3 Synthesis of zeolite supported alkaline earth metal cations doped manganese oxides catalyst:

In the volume of 50 mL deionized (DI) water, 2.0 mmol of manganese (II) acetate tetrahydrate (Mn(CH\(_3\)COO)\(_2\).4H\(_2\)O), 2.0 mmol of calcium chloride dehydrate (CaCl\(_2\).2H\(_2\)O), and 0.5 g of zeolite Na-Y (ZY) were added. The mixture solution was stirred for 24 h at room temperature. The Ca/Mn-ion exchanged (CaMn-Y) solid was filtered, washed with DI water, dried in vacuum overnight. The CaMn-Y powder was treated with 1 mmol of KMnO\(_4\) in 50 mL DI water that was stirred for 2 hours at RT followed by filtration, washing, and drying in vacuum. The color of CaMn-Y sample changed from white to brown color due to oxidation of Mn\(^{2+}\) by MnO\(_4^-\). Then oxidized sample was treated with 3.0M KCl of 50 mL solution in order to remove the residual Mn\(^{2+}\) and Ca\(^{2+}\) within the zeolites. The solution was stirred for 2 hours at RT followed by washing (~0.7 to 1 L of DI water) and drying in vacuum, and the resulting catalyst was CaMnOx-Y(Cl).

For the preparation of different alkaline earth metal ion-exchanged zeolites, 2.0 mmol of each alkaline earth metals salts such as strontium chloride hexahydrate (SrCl\(_2\).6H\(_2\)O), barium nitrate (Ba(NO\(_3\))\(_2\)), and magnesium chloride hexahydrate (MgCl\(_2\).6H\(_2\)O) were substituted for calcium salt and the same experimental procedures were followed. The catalyst containing Sr\(^{2+}\), Ba\(^{2+}\), and Mg\(^{2+}\) are abbreviated as SrMnOx-Y(Cl), BaMnOx-Y(Cl), and MgMnOx-Y(Cl) respectively.
2.1.4 Synthesis of zeolite supported alkaline earth metal cations doped manganese oxide catalyst using different anions:

The mixed solution containing 50 mL deionized (DI) water, 2.0 mmol of manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂.4H₂O), 2.0 mmol of barium Nitrate (Ba(NO₃)₂), and 0.5 g of zeolite Na-Y (ZY) were stirred for 24 h at room temperature. The Ba/Mn-ion exchanged (BaMn-Y) solid was filtered, washed with DI water, dried in vacuum overnight. The BaMn-Y powder was treated with 1 mmol of KMnO₄ in 50 mL DI water that was stirred for 2 hours at RT followed by filtration, washing, and drying in vacuum. Then oxidized was treated with 3.0M KCl of 50 mL DI water solution. The solution was stirred for 2 hours at RT followed by washing (~0.7 to 1 L of DI water) and drying in vacuum. The resulting catalyst was BaMnOx-Y(Cl). For control experiments, potassium salts KOH and KNO₃ were used. After oxidation of the catalyst using KMnO₄, KOH and KNO₃ were substituted for KCl (3.0M concentration) and the same experimental procedures were adopted. Thus the prepared catalysts using KOH and KNO₃ are designated as BaMnOx-Y(OH) and BaMnOx-Y(NO₃) respectively.

2.2 Characterization of catalysts

2.2.1 Powder X-ray Diffraction (XRD): The patterns of the catalysts including zeolite Y were characterized by Powder X-ray diffraction using Rigaku X-ray diffractometer with Cu Kα radiation. Data was collected using a 0.5 divergence and scatter slits 4 receiving slit. The scan mode was with 0.02 step size and 0.5 s dwell time.

2.2.2 Raman spectroscopy: Raman spectra were obtained for all the samples including zeolite Y using Renishaw Raman microprobe. A 633-laser line at 100% power was used for the acquisition of the spectra. The spinning cell was necessary for the collection of the
spectra in order to prevent heating of the sample and destroying its integrity. Using spinning cell helps to point the laser uniformly around the sample, thus averaging the spectra acquisition of the sample.

2.2.3 X-ray Photoelectron Spectroscopy (XPS): XPS spectra of the catalyst were obtained by utilizing Axis Kratos X-Ray Photoelectron Spectrometer. The X-ray source selected was monochromatized Al K\(_\infty\) source (12 kV, 6 mA). The region scans were acquired using 20 eV pass energy and the survey scan was obtained using 80 eV. All the peaks obtained were calibrated with respect to C 1s peak position at 285.0 eV.

2.2.4 Scanning Electron Microscope (SEM): The morphology of the samples was characterized by using FEI Helios Nanolab 600 Dual Beam Focused Ion Beam/Scanning Electron Microscope. The sample was deposited on the carbon tape and gold coated for 20 s using Metal Plasma Deposition Coater. Secondary electron microscopy images were obtained using the voltage of 20 kV.

2.2.5 Transmission Electron Microscope (TEM): The TEM of the samples was obtained using Titan3 80-3200 Probe-Corrected Monochromated at voltage of about 140 kV.

2.2.6 Energy Dispersive X-ray Analysis (EDX): The EDX of the samples was obtained using FEI Tecnai F20 S/TEM with a field emission 200kV with an X-TWIN lens
2.2.7 Elemental Analysis:

For elemental analysis of the catalyst, cold digestion method was adopted as reported in other literature\textsuperscript{86}. In a Teflon bottle, 30 mL of mixed HF, HCl and HNO\textsubscript{3} (10 mL of equal parts of each acid) was added. The catalyst (30-50 mg) was added to the acid solution. After the dissolution of the catalyst, 75 mL of 0.86M of boric acid was added to the solution in order to neutralize HF. DI water was added to the solution so that the total solution weighs 100 g. Mn\textsuperscript{2+} loading in the zeolite support was determined using Atomic Absorption Spectroscopy (AAS).

2.3 Water Oxidation Catalysis

2.3.1 Buffer preparation:

Borate buffer was prepared for the photocatalytic water oxidation. A solution of 2.62*10\textsuperscript{-3} M boric acid (H\textsubscript{3}BO\textsubscript{3}) was prepared in 250 mL DI water. Then pH of the boric acid solution was adjusted to 8.50-8.60 by using NaOH. Borate buffer of pH 5.50, 7.00, and 11.00 were prepared. A solution of 0.01 M Phosphate buffer (Na\textsubscript{2}HPO\textsubscript{4}-NaHCO\textsubscript{3}) of pH 7.00 was also used.

2.3.2 Water oxidation using Cerium Ammonium Nitrate (CAN)

A solution containing 5.485 g of CAN (0.1 M) was prepared in 100 mL DI water, the pH was in the range of 0.85-0.90. In a reactor, 80 mL of prepared CAN solution was added, and the solution was purged by N\textsubscript{2} for 10-15 minutes. In a vial 60 mg of the catalyst was dispersed with 5 mL of DI water followed by N\textsubscript{2} purging for 10-15 minutes. Then dispersed catalyst was injected in the CAN solution in the reactor, and the dissolved oxygen measurement was carried out using a fiber optic oxygen sensor.
2.3.3 Photochemical water oxidation in Ru(bpy)$_3^{2+}$/S$_2$Os$^{2-}$ system

In a photolysis reactor, 0.38 g sodium persulfate (0.02 M, 80 mL), 1.41 g sodium sulfate (0.1 M, 80 mL), 6.71 mg of tris(2,2’–bipyridyl) ruthenium chloride, 60 mg of catalyst and a borate buffer (80 ml) was added. The solution inside the reactor was sealed and purged with N$_2$ gas for 10 min while stirring. After N$_2$ purging, the reactor was illuminated with visible light using a Hg lamp equipped with a 420 nm cut-off filter and 360 mW/cm$^2$ intensity. For the measurement of dissolved oxygen evolution, YSI instruments Clark Electrode was used. The electrode was calibrated by using 100% air saturated DI water at RT (25 °C) before catalysis. The maximum concentration of dissolved oxygen in air-saturated solution is ~8 ppm. The amount of dissolved oxygen was measured by using a fiber optic oxygen sensor.

The oxygen gas evolution measurement in headspace content of the reactor was analyzed using a GC SRI 310 chromatograph equipped with a thermal conductivity detector and a 13X packed molecular sieve column. The carrier gas used was helium. The GC was calibrated using air in the room giving the direct correlation between peak area obtained and moles of O$_2$ evolved.

Control experiments were carried out with all the reagents and buffer in the reactor (parameters as mentioned above) but without catalyst, and measuring the dissolved oxygen in the system.
**Chapter 3: Results**

This section includes the synthesis, characterization, and oxygen evolution kinetics of the catalysts. Table 1 is a summary of catalysts prepared using different alkaline earth metals and different anions.

<table>
<thead>
<tr>
<th>Support</th>
<th>Mn$^{2+}$</th>
<th>N$^{2+}$</th>
<th>Treatment</th>
<th>Anions</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>No support</td>
<td>Mn$^{2+}$</td>
<td>--</td>
<td>Oxidation with KMnO$_4$</td>
<td>--</td>
<td>KCl MnOx</td>
</tr>
<tr>
<td><strong>Zeolite supported manganese oxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite</td>
<td>Mn$^{2+}$</td>
<td>--</td>
<td>Ion exchanging of cations and Oxidation with KMnO$_4$</td>
<td>MnOx-Y*</td>
<td>KCl MnOx-Y(Cl)</td>
</tr>
<tr>
<td><strong>Zeolite supported alkaline earth metal cations doped manganese oxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite</td>
<td>Mn$^{2+}$</td>
<td>Ba$^{2+}$</td>
<td>Ion exchanging of cations and Oxidation with KMnO$_4$</td>
<td>--</td>
<td>KCl BaMnOx-Y(Cl)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Mn$^{2+}$</td>
<td>Sr$^{2+}$</td>
<td></td>
<td>KCl</td>
<td>SrMnOx-Y(Cl)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Mn$^{2+}$</td>
<td>Ca$^{2+}$</td>
<td></td>
<td>KCl</td>
<td>CaMnOx-Y(Cl)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Mn$^{2+}$</td>
<td>Mg$^{2+}$</td>
<td></td>
<td>KCl</td>
<td>MgMnOx-Y(Cl)</td>
</tr>
<tr>
<td><strong>Zeolite supported alkaline earth metal cations doped manganese oxides and treated with different anion</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Zeolite</td>
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<td>Ba$^{2+}$</td>
<td>Ion exchanging of cations and Oxidation with KMnO$_4$</td>
<td>--</td>
<td>KOH BaMnOx-Y(OH)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Mn$^{2+}$</td>
<td>Ba$^{2+}$</td>
<td></td>
<td>KNO$_3$</td>
<td>BaMnOx-Y(NO$_3$)</td>
</tr>
</tbody>
</table>

Table 1: Abbreviation of different zeolite-supported and non-supported manganese oxides
The characterizations of the materials in Table 1 was done using Atomic Absorption Spectroscopy (AAS), X-ray diffraction pattern (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Scanning Electron Microscopy (SEM), and High-resolution Transmission Electron Microscopy (HRTEM).

Scheme for the synthesis of zeolite supported manganese oxides involves three main steps:

1. Ion exchange of cations: For the synthesis of manganese oxides catalysts, Mn$^{II}$ ions were ion-exchanged into zeolite Y framework at room temperature. For the zeolite supported alkaline earth metal cations doped manganese oxides, both Mn$^{2+}$/alkaline earth metal cations (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) were ion-exchanged simultaneously.

2. Precipitation of ion exchanged ions on the zeolite surface: These ion-exchanged zeolite sample are treated with KMnO$_4$ at room temperature. K$^+$ cations ion-exchange intrazeolitic cations and MnO$_4^-$ oxidizes Mn$^{2+}$ and Mn$^{2+}$/alkaline earth metal cations (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$), which results the precipitation of manganese oxides on the surface of zeolite.

3. Treatment with potassium salts: In order to remove residual Mn$^{II}$ or Mn$^{II}$/alkaline earth metal cations inside zeolite cage, zeolite supported manganese oxides is treated with high concentration of potassium salts KCl or KNO$_3$ or KOH after step 2.
The schematic representation of synthesis of zeolite supported manganese oxides are shown in Figure 7 and 8. In order to synthesize alkaline earth metal cations doped manganese oxides, respective alkaline earth metal cations are mixed with manganese ions during ion exchanging of zeolite.

Figure 7: Schematic representation of the synthesis of catalyst. light blue: (Na⁺, counter balance cation in zeolite framework), dark blue: (Ion-exchanging cations: Mn²⁺ or Mn³⁺/alkaline earth metal cations, light yellow: catalyst precipitated on the surface of zeolite
3.1 Elemental Analysis of Prepared Catalysts

The samples for AAS characterization were prepared using HF cold digestion method. The Mn content of all samples was determined by using AAS. The loadings of alkaline earth metal cations in the zeolite were not determined. The Mn content of the samples is shown in Table 2 below:
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mn (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manganese oxide</strong></td>
<td></td>
</tr>
<tr>
<td>MnOx</td>
<td>49.4</td>
</tr>
<tr>
<td><strong>Zeolite-supported manganese oxides</strong></td>
<td></td>
</tr>
<tr>
<td>MnOx-Y(Cl)</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>Zeolite-supported alkaline earth metal cations doped manganese oxide</strong></td>
<td></td>
</tr>
<tr>
<td>BaMnOx-Y(Cl)</td>
<td>1.2</td>
</tr>
<tr>
<td>SrMnOx-Y(Cl)</td>
<td>2.2</td>
</tr>
<tr>
<td>CaMnOx-Y(Cl)</td>
<td>2.7</td>
</tr>
<tr>
<td>MgMnOx-Y(Cl)</td>
<td>5.4</td>
</tr>
<tr>
<td><strong>Zeolite supported alkaline earth metal cations doped manganese oxides and influence of cations</strong></td>
<td></td>
</tr>
<tr>
<td>BaMnOx-Y(OH)</td>
<td>1.6</td>
</tr>
<tr>
<td>BaMnOx-Y(NO₃)</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 2: Manganese loadings in manganese oxides (MnOx), zeolite–supported manganese oxides (MnOx-Y(Cl)), zeolite supported alkaline earth metal cations doped manganese oxides (MgMnOx-Y(Cl), CaMnOx-Y(Cl), SrMnOx-Y(Cl), BaMnOx-Y(Cl)), zeolite supported alkaline earth metal cations doped manganese oxides and treated with different anions (BaMnOx-Y(OH), BaMnOx-Y(NO₃)) determined from AAS.
3.2 Powder X-ray Diffraction Pattern (XRD)

3.2.1 Zeolite:

The X-ray diffraction patterns for zeolite Y (ZY) are shown in Figure 9. Zeolite framework is not stable in low pH conditions. When zeolite is exposed to cerium ammonium nitrate CAN (0.10M, pH 0.9), the zeolitic framework is destroyed due to leaching of aluminum, which is supported by XRD diffraction of zeolite treated with CAN (ZY-CAN) shown in Figure 9. The XRD of ZY-CAN show that zeolite becomes amorphous after treatment with CAN.

3.2.2 Manganese oxides:

The X-ray diffraction patterns for manganese oxides (MnOx) are shown in Figure 10. Three broad peaks at around $2\theta \sim 24^\circ$, $36.5^\circ$ and $66^\circ$ were detected in the sample.

3.2.3 Zeolite supported manganese oxides:

Zeolite Y (ZY) diffraction patterns are strong which dwarfed the other crystalline peaks of catalyst (if present). Thus some of the peaks were zoomed in order to determine the d-spacings of the crystalline faces of the catalysts.

For the sample MnOx-Y(Cl)*, the XRD patterns did not show any additional prominent peaks apart from zeolite peaks as shown in Figure 11, 12, and 13. After treatment with KCl, the crystalline peaks of manganese oxides were observed for the sample MnOx-Y(Cl). The peaks were observed at 2 theta ($2\theta$) at $12.5^\circ$ ($\sim 7$ A$^\circ$), $24^\circ$ ($\sim 3.5$ A$^\circ$), and $36^\circ$ ($\sim 2.5$ A$^\circ$) as shown in Figure 11, 12, and 13.

3.2.4 Zeolite supported alkaline earth metal cations doped manganese oxides
The XRD crystalline peaks for alkaline earth metal cations doped manganese oxides manganese oxides were studied. The XRD peaks were observed at 2 theta (2θ) at 12.5° (~7 Å), 24° (~3.5 Å), 36° (~2.5Å), and 39° (~2Å) for the catalysts MgMnOx-Y(Cl), CaMnOx-Y(Cl), SrMnOx-Y(Cl), and BaMnOx-Y(Cl) as shown in Figure 14, 15, and 16.

3.2.5 Zeolite supported alkaline earth metal cations doped manganese oxides and the influence of different anions

After ion-exchanged zeolite was treated with KMnO₄, the sample was treated with different potassium salts: KCl, KOH and KNO₃ (BaMnOx-Y(Cl), BaMnOx-Y(OH) and BaMnOx-Y(NO₃) respectively). After treatment with KNO₃ potassium salts, the XRD peaks at 2theta (2θ) at 12.5° (~7 Å), 24° (~3.5 Å), and 36° (~2.5Å) were observed as shown in Figure 17, 18, and 19. However, the peaks of manganese oxides found in the sample BaMnOx-Y(NO₃) were not observed in the sample BaMnOx-Y (OH).

3.3 Raman Spectroscopy

Raman scattering spectra of prepared catalyst were obtained. Zeolite Y (ZY) showed a strong peak at 500cm⁻¹ as shown in Figure 2.7 (summarized in Table 3). Additional peaks were observed at the range of 550-650cm⁻¹ range which refers to manganese oxides peaks.

3.3.1 Manganese oxides:

For the sample manganese oxides MnOx, experimental results showed three Raman scattering peaks as shown in Figure 20 (summarized in Table 3). The two energy bands at 572 and 650 cm⁻¹ have strong intensity. However the lower-frequency band at 500 cm⁻¹ appear weak intensity relative to those two former high frequency bands.
3.3.2 Zeolite supported manganese oxides:

There were two strong Raman scattering peaks at 571 cm\(^{-1}\) and 650 cm\(^{-1}\) observed in manganese oxides after treating with KMnO\(_4\) (MnOx-Y*). After treatment with KCl, there were no any changes in the intensities of those peaks. The peak intensity of 650 cm\(^{-1}\) was greater relative to that of 573 cm\(^{-1}\) peak. The low frequency band at ~500 cm\(^{-1}\) was attributed to zeolite vibrations as shown in Figure 21 (summarized in Table 3).

3.3.3 Zeolite supported alkaline earth metal cations doped manganese oxides

Raman scattering peaks were analyzed for zeolite supported alkaline earth metal cations doped manganese oxides as shown in Figure 22. In case of MgMnOx-Y(Cl), there were two peaks observed at 567 and 648 cm\(^{-1}\) and for CaMnOx-Y(Cl) there were observed at 570 and 649 cm\(^{-1}\), in which high energy band was weaker in intensity relative to low energy band. In case of SrMnOx-Y(Cl) sample, the peak intensities of two bands 571 and 651 cm\(^{-1}\) were similar. For the sample BaMnOx-Y(Cl), there was a strong peak at 574 cm\(^{-1}\) but the peak at 652 cm\(^{-1}\) was intense compared to low energy band. In all samples, two intense peaks were observed ~570 and ~650 cm\(^{-1}\) as summarized in Table 3.

3.3.4 Zeolite supported alkaline earth metal cations doped manganese oxides and the influence of different anions

In Figure 23, Raman spectra are shown for different catalysts: BaMnOx-Y(Cl) (Cl), BaMnOx-Y (OH), and BaMnOx_Y (NO\(_3\)). As mentioned earlier, BaMnOx-Y(Cl) (Cl) sample had a weak band at 574 cm\(^{-1}\) and strong peak at 652 cm\(^{-1}\). In case of BaMnOx-Y(NO\(_3\)), two strong bands were observed at 571 cm\(^{-1}\) and 650 cm\(^{-1}\). However, in BaMnOx-Y (OH) sample, both bands 576 cm\(^{-1}\) and 652 cm\(^{-1}\) were present but weak in intensity and broadened.
### Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Raman scattering energy bands (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manganese oxide</strong></td>
<td></td>
</tr>
<tr>
<td>MnOx</td>
<td>500, 572, 650</td>
</tr>
<tr>
<td><strong>Zeolite-supported manganese oxides</strong></td>
<td></td>
</tr>
<tr>
<td>MnOx-Y(Cl)</td>
<td>502, 573, 650</td>
</tr>
<tr>
<td><strong>Zeolite-supported alkaline earth metal cations doped manganese oxide</strong></td>
<td></td>
</tr>
<tr>
<td>MgMnOx-Y(Cl)</td>
<td>502, 567, 648</td>
</tr>
<tr>
<td>CaMnOx-Y(Cl)</td>
<td>499, 570, 649</td>
</tr>
<tr>
<td>SrMnOx-Y(Cl)</td>
<td>498, 571, 651</td>
</tr>
<tr>
<td>BaMnOx-Y(Cl)</td>
<td>496, 574, 652</td>
</tr>
<tr>
<td><strong>Zeolite supported alkaline earth metal cations doped manganese oxides and influence of cations</strong></td>
<td></td>
</tr>
<tr>
<td>BaMnOx-Y(OH)</td>
<td>496, 576, 652</td>
</tr>
<tr>
<td>BaMnOx-Y(NO(_3))</td>
<td>498, 571, 650</td>
</tr>
</tbody>
</table>

Table 3: Raman scattering spectra of manganese oxides (MnOx), zeolite–supported manganese oxides (MnOx-Y(Cl)), zeolite supported alkaline earth metal cations doped manganese oxides (MgMnOx-Y(Cl), CaMnOx-Y(Cl), SrMnOx-Y(Cl), BaMnOx-Y(Cl)), zeolite supported alkaline earth metals cations doped manganese oxides and treated with different anions (BaMnOx-Y(OH), BaMnOx-Y(NO\(_3\)))

### 3.4 X-ray Photoelectron Spectroscopy (XPS)

For the determination of oxidation states of manganese in the sample surface, Mn 2p\(_{3/2}\) binding energy is important. The binding energies of Mn 2p\(_{3/2}\) were determined by peak fitting deconvolutions.

#### 3.4.1 Manganese oxides:

The XPS peaks for MnOx were observed at binding energies 643.0 and 642.5 eV, and shoulder at 641.3 eV as shown in Figure 24 (summarized in Table 4).
3.4.2 Zeolite supported manganese oxides:

The XPS spectrum for Mn 2p spin orbit splitting for sample MnOx-Y (Cl) are shown in Figure 25. For the sample MnOx-Y(Cl), the binding energy for Mn 2p$_{3/2}$ peaks was at 642.5 eV (summarized in Table 4).

3.3.5 Zeolite supported alkaline earth metal cations doped manganese oxides:

The XPS spectra of zeolite supported alkaline earth metal cations doped manganese oxides were studied. MgMnOx-Y(Cl) sample has a strong binding energy at 643.0 eV and a shoulder at 641.3 eV (Figure 26). CaMnOx-Y(Cl) sample has a strong binding energy at 641.7 eV and a shoulder at 643.2 eV (Figure 27). For the sample SrMnOx-Y(Cl), there were three peaks by deconvolutions: 643.4, 642.4 eV and 641.0 eV (Figure 28). BaMnOx-Y(Cl) sample also showed three binding energies: 643.0, 642.4, and 641.1 eV (Figure 29). All the XPS binding energies of the catalysts are summarized below in Table 4.

3.3.6 Zeolite supported alkaline earth metal cations doped manganese oxides and the influence of anions:

The XPS spectra of barium metal cations doped manganese oxides treated with different anions were studied. In case of KOH treated barium cations doped manganese oxides (BaMnOx-Y (OH)), there was a strong binding energy at 642.3 eV as shown in Figure 30. On the other hand, KNO$_3$ treated barium cations doped manganese oxides (BaMnOx-Y(NO$_3$)), there were three peaks at binding energies 643.3, 642.6, and 641.1 eV as shown in Figure 31. The results of XPS studies are summarized in Table 4 below:
<table>
<thead>
<tr>
<th>Samples</th>
<th>XPS peaks (Binding energies, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn2p3/2</td>
</tr>
<tr>
<td>Manganese oxide</td>
<td></td>
</tr>
<tr>
<td>MnOx</td>
<td>643.0, 642.5, 641.3</td>
</tr>
<tr>
<td>Zeolite-supported manganese oxides</td>
<td></td>
</tr>
<tr>
<td>MnOx-Y(Cl)</td>
<td>642.7</td>
</tr>
<tr>
<td>Zeolite-supported alkaline earth metal cations doped manganese oxide</td>
<td></td>
</tr>
<tr>
<td>MgMnOx-Y(Cl)</td>
<td>643.0, 642.5, 641.3</td>
</tr>
<tr>
<td>CaMnOx-Y(Cl)</td>
<td>643.2, 641.7</td>
</tr>
<tr>
<td>SrMnOx-Y(Cl)</td>
<td>643.4, 642.4, 641.0</td>
</tr>
<tr>
<td>BaMnOx-Y(Cl)</td>
<td>642.9, 642.4, 641.1</td>
</tr>
<tr>
<td>Zeolite supported alkaline earth metals cations doped manganese oxides and influence of cations</td>
<td></td>
</tr>
<tr>
<td>BaMnOx-Y(OH)</td>
<td>642.3</td>
</tr>
<tr>
<td>BaMnOx-Y(NO₃)</td>
<td>643.3, 642.6, 641.1</td>
</tr>
</tbody>
</table>

Table 4: XPS binding energy of Mn2p3/2 of manganese oxides (MnOx), zeolite – supported manganese oxides (MnOx-Y(Cl)), zeolite supported alkaline earth metal cations doped manganese oxides (MgMnOx-Y(Cl), CaMnOx-Y(Cl), SrMnOx-Y(Cl), BaMnOx-Y(Cl)), zeolite supported alkaline earth metals cation doped manganese oxides and treated with different anions (BaMnOx-Y(Cl)(OH), BaMnOx-Y(Cl)(NO₃))
3.5 Scanning electron microscopy (SEM) images

Manganese oxides (MnOx) samples were random in shape and size. They formed like a cluster as shown in Figure 34. They ranged from nanosize (~500 nm) to micron size (~2-3 μm) as shown in Figure 34 and 35.

The size of zeolite Y crystal is of the order of one micron as seen in Figure 36. Nanosized catalyst are deposited on zeolite Y. MnOx-Y(Cl) (Figure 36), MgMnOx-Y(Cl) (Figure 37), CaMnOx-Y(Cl) (Figure 38), SrMnOx-Y(Cl) (Figure 39), and BaMnOx-Y(Cl) (Figure 40) are nanosized clusters deposited on the zeolite surface. The deposits were random in shape and different in size among different alkaline earth metal cations doped in manganese oxides. They looked widely dispersed on the surface of support. The abundance of the catalyst on the zeolite surface was in the following order: MnOx-Y(Cl) (Cl) ~ MgMnOx-Y(Cl) > CaMnOx-Y(Cl) ~ SrMnOx-Y(Cl) >> BaMnOx-Y(Cl). The size of these samples ranged from 50-80 nm in length and 15-20 nm in width.

SEM images were obtained for barium cations doped manganese oxides treated with salts KNO₃ and KOH: BaMnOx-Y(NO₃) and BaMnOx-Y (OH) respectively. Both samples have a minimal amount of catalysts on the zeolite surface, but the catalysts were comparatively larger in size than other catalysts as shown in Figure 41 for BaMnOx-Y(NO₃) and in Figure 42 for BaMnOx-Y (OH). They were in the range of 50-80 nm in size.
SEM images were taken for the sample SrMnOx-Y(Cl) after photolysis in borate buffer in the pH 8.5 (shown in Figure 43), and they both showed that zeolite support was intact and there was no significant change in the morphology of the catalyst.

3.6 **High resolution transmission electron microscope (HR-TEM)**

The TEM micrograph of SrMnOx-Y(Cl) and BaMnOx-Y(Cl) sample showed that nano-sized clusters of 40-70 nm sizes are anchored to zeolite support (Figure 44 and 45). The HR TEM of the sample showed that catalysts have fringes and are not amorphous. Through FFT analysis, TEM showed that catalyst are nanocrystalline with d-spacing of 2.5 Å and 3.5 Å in both samples SrMnOx-Y(Cl) and BaMnOx-Y(Cl) as shown in Figure 44 and 45 respectively.

3.7 **Energy dispersive X-ray analysis**

EDX analysis spectra were analyzed for the sample BaMnOx-Y(Cl) as shown in Figure 46. It shows that the sample has both barium and manganese present on the zeolite. There is Mn Kα peak around 5.89 eV along with comparatively a smaller peak of Ba Lα at around 4.47 eV. There was strong peak for K Kα at 3.312 eV. There was also peak for Cl Kα at around 2.62 eV.

3.8 **Water oxidation catalysis**

3.8.1 **Chemical water oxidation by zeolite supported manganese oxides in cerium ammonium nitrate (CAN)**

Water oxidation using MnOx-Y(Cl) was done in presence of CAN (0.1M, pH 0.89). The catalyst was reused again without further washing (2nd run: first recovery, 3rd run: second recovery), and the TOF of the catalyst decreased significantly compared to fresh catalyst
as shown in Figure 47. The summary of the rate and TOF of oxygen evolution is shown below in Table 5:

<table>
<thead>
<tr>
<th>MnOx-Y(Cl)/CAN</th>
<th>Rate (μmol/s)</th>
<th>TOF (mmolO2mol−1MnS−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st run</td>
<td>5.3 * 10⁻²</td>
<td>0.96</td>
</tr>
<tr>
<td>2nd run</td>
<td>1.3 * 10⁻²</td>
<td>0.24</td>
</tr>
<tr>
<td>3rd run</td>
<td>9.0 * 10⁻³</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 5: Summary of dissolved oxygen evolution kinetics of zeolite supported manganese oxides catalyst suspended in CAN (0.1M) solution. (1st run: first photolytic water oxidation test; 2nd run: first recovery test; 3rd run: second recovery test)

### 3.8.2 Photochemical water oxidation by zeolite supported manganese oxides using Ru(bpy)₃²⁺/S₂O₈²⁻ photocatalytic system

#### 3.8.2.1 Buffer effect on photochemical water oxidation by zeolite supported manganese oxides

The catalytic activity of MnOx-Y(Cl) was measured in phosphate buffer (0.01 M, pH 7.00). Figure 48 shows that TOF of dissolved oxygen evolution kinetics for first run was 0.46 mmolO₂mol⁻¹MnS⁻¹. The catalyst was recovered directly from the reaction mixture and reused without washing. In the second run, the catalytic activity of MnOx-Y(Cl) was 0.44 mmolO₂mol⁻¹MnS⁻¹. The catalyst was used for third run and the TOF of the catalyst decreased to 0.36 mmolO₂mol⁻¹MnS⁻¹. The light driven photocatalytic water oxidation by MnOx-Y(Cl) was measured in borate buffer (2.67 * 10⁻³ M, pH 8.5). The MnOx-Y(Cl) sample had the TOF of 1.75 mmolO₂mol⁻¹MnS⁻¹ in the first run of water photolysis, and TOF of 1.82 mmolO₂mol⁻¹MnS⁻¹ in two consecutive runs as shown in
Figure 49. The dissolved oxygen evolution kinetics of the sample MnOx-Y(Cl) in phosphate and borate buffer systems are summarized in Table 6 below:

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Sample MnOx-Y(Cl)</th>
<th>Rate (μmols⁻¹)</th>
<th>TOF (mmol O₂mol⁻¹Mn⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate pH 7.00</td>
<td>1ˢᵗ run</td>
<td>2.5 * 10⁻²</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>2ⁿᵈ run</td>
<td>2.4 * 10⁻²</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>3ʳᵈ run</td>
<td>2.0 * 10⁻²</td>
<td>0.36</td>
</tr>
<tr>
<td>Borate</td>
<td>1ˢᵗ run</td>
<td>9.6 * 10⁻²</td>
<td>1.75</td>
</tr>
<tr>
<td>pH 8.50</td>
<td>2ⁿᵈ run</td>
<td>0.10</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>3ʳᵈ run</td>
<td>0.10</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Table 6: Summary of dissolved oxygen evolution kinetics of fresh and recovered zeolite supported manganese oxides MnOx-Y(Cl) in phosphate buffer (pH 7.00) and borate buffer (pH 8.50) in Ru(bpy)₃²⁺/S₂O₈²⁻ photocatalytic system (1ˢᵗ run: first photolytic water oxidation test; 2ⁿᵈ run: first recovery test; 3ʳᵈ run: second recovery test)

3.8.2.2 pH effect on photochemical water oxidation by zeolite supported manganese oxides

The catalytic activity of the catalyst was also detected in different pH range of borate buffer. For this experiment borate buffer of pH 5.50, 7.00, 8.50, and 11.00 were prepared, and the following trend was observed in catalytic activity: pH 8.50 > 7.00 > 5.00 as shown in Figure 50 (summarized in Table 7 below). The dissolved oxygen evolution kinetics of MnOx-Y(Cl) in borate buffer pH 5.00, 7.00, 8.50 was 0.031, 0.18,
and 1.75 mmol$_{O_2}$mol$_{-1}$Mn$_{s}^{-1}$ respectively. There was no oxygen evolution at pH 11.00 borate buffer system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Borate buffer (pH)</th>
<th>Rate (µmol s$^{-1}$)</th>
<th>TOF (mmol$<em>{O_2}$mol$</em>{-1}$Mn$_{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnOx$_Y$(Cl)</td>
<td>5.0</td>
<td>1.7 * 10$^{-3}$</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>9.7 * 10$^{-3}$</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>9.6 * 10$^{-2}$</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 7: Summary of dissolved oxygen evolution kinetics of zeolite supported manganese oxides MnOx$_Y$(Cl) in different pH (5.0, 7.0, 8.5, 11.0) of borate buffer in Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ photocatalytic system

### 3.8.2.3 Role of zeolite support in photochemical water oxidation

Water oxidation of the rest of the samples were studied in Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ photocatalytic system in borate buffer (pH 8.50). There was no oxygen evolution in absence of zeolite-supported catalyst in the system. The rate of oxygen evolution for the zeolite supported manganese oxides MnOx$_Y$(Cl) and non-supported manganese oxides MnOx were compared in Figure 51. The dissolved oxygen evolution kinetic studies of MnOx$_Y$(Cl) were with TOF of 1.75 mmol$_{O_2}$mol$_{-1}$Mn$_{s}^{-1}$, and that of MnOx was 0.14 mmol$_{O_2}$mol$_{-1}$Mn$_{s}^{-1}$ as summarized in Table 8 below:
### Table 8: Summary of dissolved oxygen evolution kinetics of zeolite supported manganese oxides (MnOx-Y(Cl)) and non-supported manganese oxides (MnOx) in borate buffer (pH 8.50) in Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ photocatalytic system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate (µmol/s)</th>
<th>TOF (mmol$<em>{O_2}$/mol$</em>{Mn}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnOx-Y(Cl)</td>
<td>9.6 * 10$^{-2}$</td>
<td>1.75</td>
</tr>
<tr>
<td>MnOx</td>
<td>2.6 * 10$^{-2}$</td>
<td>0.14</td>
</tr>
</tbody>
</table>

#### 3.8.2.4 Role of high concentration of K$^+$ ions in photochemical water oxidation by zeolite supported manganese oxides

Figure 52 compares the catalytic activity of the MnOx-Y* and MnOx-Y(Cl). The dissolved oxygen evolution kinetic studies of MnOx-Y(Cl)* were with TOF of 0.28 mmol$_{O_2}$/mol$_{Mn}$s$^{-1}$, and that of MnOx-Y(Cl) was 1.75 mmol$_{O_2}$/mol$_{Mn}$s$^{-1}$ as summarized in Table 9 below:

### Table 9: Summary of dissolved oxygen evolution kinetics of zeolite supported manganese oxides before (MnOx-Y*) and after KCl treatment (MnOx-Y(Cl)) in borate buffer (pH 8.50) in Ru(bpy)$_3^{2+}$/S$_2$O$_8^{2-}$ photocatalytic system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate (µmols$^{-1}$)</th>
<th>TOF (mmol$<em>{O_2}$/mol$</em>{Mn}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnOx-Y*</td>
<td>1.8 * 10$^{-2}$</td>
<td>0.28</td>
</tr>
<tr>
<td>MnOx-Y(Cl)</td>
<td>9.6 * 10$^{-2}$</td>
<td>1.75</td>
</tr>
</tbody>
</table>

#### 3.8.2.5 Photochemical oxygen evolution kinetics of zeolite supported alkaline earth metal cations doped manganese oxides:

Figure 53 compares the catalytic activities of zeolite-supported alkaline earth metals doped manganese oxides catalysts by normalizing the Mn content in the catalyst,
it showed the following trending order: BaMnOx-Y(Cl) > SrMnOx-Y(Cl)> CaMnOx-
Y(Cl) > MgMnOx-Y(Cl). The catalyst BaMnOx-Y(Cl) demonstrated the highest catalytic activity of water oxidation, and the least catalytic activity was of MgMnOx-Y(Cl). The dissolved oxygen evolution kinetics of water oxidation catalytic rate are discussed in Table 10 below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate (μmol/s)</th>
<th>TOF (mmolO2.molMn⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaMnOx-Y(Cl)</td>
<td>9.5 * 10⁻²</td>
<td>7.21</td>
</tr>
<tr>
<td>SrMnOx-Y(Cl)</td>
<td>8.9 * 10⁻²</td>
<td>4.10</td>
</tr>
<tr>
<td>CaMnOx-Y(Cl)</td>
<td>8.5 * 10⁻²</td>
<td>2.90</td>
</tr>
<tr>
<td>MgMnOx-Y(Cl)</td>
<td>8.4 * 10⁻²</td>
<td>1.43</td>
</tr>
<tr>
<td>MnOx-Y(Cl)</td>
<td>9.6 * 10⁻²</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 10: Summary of dissolved oxygen evolution kinetics of zeolite supported manganese oxides and alkaline earth metal cations-doped manganese oxides in borate buffer (pH 8.5) in Ru(bpy)₃²⁺/S₂O₅²⁻ photocatalytic system

The barium cations doped manganese oxides (BaMnOx-Y(Cl)) samples were the most active water oxidizing catalysts among other samples. Two new samples of BaMnOx-Y(Cl) were prepared to reproduce the results. The average TOFs of these samples were 6.75 ± 0.69 mmolO₂.molMn⁻¹s⁻¹ as shown in Figure 54.
Sample | Trials | Rate (μmol/s) | TOF (mmolO₂.mol⁻¹Mn⁻¹s⁻¹) | Average TOF (mmolO₂.mol⁻¹Mn⁻¹s⁻¹)
---|---|---|---|---
BaMnOx-Y(Cl) | 1ˢᵗ | 9.5 × 10⁻² | 7.21 | 6.75 ± 0.69
| 2ⁿᵈ | 8.6 × 10⁻² | 7.09 | 
| 3ʳᵈ | 8.3 × 10⁻² | 5.96 | 

Table 11: Summary of dissolved oxygen evolution kinetics of three different samples of zeolite supported barium cations doped manganese oxides in borate buffer (pH 8.5) in Ru(bpy)_3²⁺/S₂O₈²⁻ photocatalytic system

The photolytic water oxidation to molecular oxygen by zeolite-supported barium metal cations doped manganese oxides BaMnOx-Y(Cl) was detected by GC as shown in Figure 55. The oxygen evolved in the headspace of reactions was measured to be 6.31 mmolO₂.mol⁻¹Mn⁻¹s⁻¹.

3.8.2.6 Photochemical oxygen evolution kinetics of zeolite supported alkaline earth metal cations manganese oxides and the influence of different anions

The most active catalyst barium metal cations doped manganese oxides were treated with different anions KCl, KOH, and KNO₃ salts and the respective samples were prepared as following: BaMnOx-Y(Cl), BaMnOx-Y (OH), and BaMnOx-Y (NO₃). Figure 56 demonstrates the catalytic activity was in the following order: BaMnOx-Y(Cl) > BaMnOx-Y(NO₃) > BaMnOx-Y (OH). The rates of dissolved oxygen evolution in TOFs of these samples are summarized in Table 12 below:
<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate (μmol-s⁻¹)</th>
<th>TOF (mmolO₂-molMn⁻¹-s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaMnOx-Y(Cl)</td>
<td>9.5 * 10⁻²</td>
<td>7.21</td>
</tr>
<tr>
<td>BaMnOx-Y (OH)</td>
<td>8.2 * 10⁻²</td>
<td>4.67</td>
</tr>
<tr>
<td>BaMnOx-Y (NO₃)</td>
<td>1.0 * 10⁻¹</td>
<td>5.93</td>
</tr>
</tbody>
</table>

Table 12: Summary of zeolite supported alkaline earth metal cations based manganese oxide catalysts treated with different anions in borate buffer (pH 8.5-8.6) in Ru(bpy)₃²⁺/S₂O₅²⁻ photocatalytic system (KCl: BaMnOx-Y(Cl); KOH: BaMnOx-Y (OH); KNO₃: BaMnOx-Y(NO₃))

3.8.2.7 Determination of photosensitizer Ru(bpy)₃²⁺ concentration under photochemical conditions

The concentration of Ru(bpy)₃²⁺ in the photochemical reaction mixture Ru(bpy)₃²⁺-persulfate was measured before and after photolysis of water using diffuse reflectance as shown in Figure 57. The concentration of Ru(bpy)₃²⁺ was measured by monitoring MLCT absorption band in the range of 400-500 nm. The photochemical water oxidation carried out using BaMnOx-Y(Cl) in high alkaline condition using borate buffer (pH 8.5). Figure 57 shows that the absorbance band of Ru(bpy)₃²⁺ decreases significantly after photolysis under above mentioned photochemical conditions (red-before photolysis; black-after photolysis).
Figure 9: XRD patterns for Zeolite-Y (ZY) and ZY after CAN (0.10 M) treatment (ZY-CAN)
Figure 10: XRD patterns for manganese oxides without any support (MnOx)
Figure 11: XRD patterns ($2\theta = 11^\circ$-$14^\circ$) for zeolite supported manganese oxides: MnOx-Y* and MnOx-Y(Cl)

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4.1 Importance of zeolite support for water oxidation catalysis:

Manganese dioxides are formed by the disproportionation reaction of Mn$^{II}$ and potassium permanganate ($\text{MnO}_4^-$) as shown below:

\[
2\text{MnO}_4^- (aq) + 3\text{Mn}^{2+} (aq) + 2\text{H}_2\text{O}(l) \rightarrow 5\text{MnO}_2 (s) + 4\text{H}^+ (aq)^{87}
\]

Manganese oxides, in general, exhibit mainly two types of structures: tunnel shaped octahedral framework and layered structure$^{88}$. In tunnel shaped structure, edge-sharing MnO$_6$ octahedra chains share corners to from tunnel structures that are parallel to the chains$^2$. Layered manganese oxides are constructed by edge sharing of MnO$_6$ octahedra to from sheets with cations and water molecules between adjacent sheets$^{89}$. The O-H-O bonds bind the layers of MnO$_6$ octahedral sheets, and thus hydroxyl bond is an integral part of the layered structure of manganese oxides structure$^{88}$. Here we investigate the structural characteristics of manganese oxides.

4.1.1 Structural characterization of manganese oxides with or without zeolite support

Manganese oxides (MnOx) catalyst was synthesized by using manganese acetate as a precursor and oxidized by potassium permanganate. The reflections obtained by powder X-ray diffraction showed that the synthesized MnOx catalyst is amorphous in nature with broad peaks at 2$\theta$ ~ 24º (3.5 Å), 36º (2.5 Å), and 66º (1.5 Å) which arises from 002, 100, and 110 reflections respectively. The PXRD patterns (Figure 10)
resemble hexagonal birnessite (layered like structure)\textsuperscript{90,91,92}. Mineral sheets with hexagonal layer symmetry and a significant proportion of reactive anionic vacancy sites characterize the hexagonal birnessite\textsuperscript{93,94}. The broadening of basal reflection (002) and weak intensity indicate the randomness in the stacking of layered sheets\textsuperscript{93}. Since the peaks appearing at higher angle are also broad, which indicate that there is a high turbostraticity in stacking of layered manganese oxides\textsuperscript{55}.

Zeolite supported manganese oxides were prepared by oxidizing Mn\textsuperscript{2+} ion-exchanged zeolite Y oxidized by potassium permanganate. In case of zeolite supported manganese oxides after permanganate treatment (MnOx-Y\textsuperscript{*}), there were no additional XRD reflections other than zeolite crystalline peaks (Figure 11, 12, 13) which means the sample was completely amorphous. After treatment of MnOx-Y\textsuperscript{*} with high concentration of potassium chloride (KCl) salt, the sample MnOx-Y(Cl) have new XRD peaks at 2\(\theta\) ~ 12.5\(^{\circ}\) (7A\(^{\circ}\)), 24\(^{\circ}\) (3.5 A\(^{\circ}\)), and 36\(^{\circ}\) (2.5 A\(^{\circ}\)), distinct from the zeolite peaks as shown in Figure 11, 12, 13. The peaks observed at 12.5\(^{\circ}\) and 24\(^{\circ}\) corresponds to basal 001 and 002 reflection respectively\textsuperscript{55,95}, which indicate the alignment of MnO\(_6\) layers parallel to the (a,b) planes\textsuperscript{91}. The broadening of these peaks suggest that manganese oxides deposited on the zeolite surface are amorphous, poorly ordered birnessite like manganese oxides sheets analogous to hexagonal birnessites\textsuperscript{92,96}. They are arranged in a random fashion similar to K-\(\delta\)-MnO\(_2\) nanosheets where K\textsuperscript{+} ions occupy the alternating positions of manganese oxides layers\textsuperscript{97}. The birnessite crystalline polymorph of manganese oxides is similar to the structure of K-\(\delta\)-MnO\(_2\), but different only in basal spacing (\(\delta\)-MnO\(_2\), c = 4.7 A\(^{\circ}\)) of the MnO\(_2\) layers\textsuperscript{96}. The birnessite are hexagonal unit cell with a = 2.84 A\(^{\circ}\) equivalent to
the edge length of the MnO$_6$ octahedra and $c = 7 \text{ Å}$ similar to distance between the
adjacent octahedral layers featured with (1x $\infty$) layered structure.$^{98}$ The spacing of those
MnO$_2$ layers is determined by the size and occupancy of cations found between the
adjacent layers of MnO$_2$ layers$^{97}$. Since the basal spacings of MnOx-Y(Cl) are broadened
and weak in intensities, this suggests the destabilization of layered structure of MnO$_2$
layers with structural defects in lattice.$^{94}$

Raman scattering spectra for MnOx showed three Raman scattering peaks at 500, 572 and 650 cm$^{-1}$ frequency regions, with the two latter peaks being intense (Figure 20). It has been reported that birnessite type MnO$_2$ are featured with Raman active modes at 500-515, 575-585, and 625-650 cm$^{-1}$,$^{98}$ where the two high frequency bands are strong, while the low frequency band is of a weak intensity. Three similar frequencies were also observed in MnOx-Y* and MnOx-Y(Cl) samples, however, the peak around 500 cm$^{-1}$ found in these samples is arising from T-O-T stretching of zeolite Y (T= Al, Si)$^{99}$ (Figure 21). In birnessite, MnO$_6$ octahedral layers contain a vacancy in one over every six
octahedral sites, which are counterbalanced by mono- or di-valent cations along with
water molecules present in interlayers of MnO$_6$ extended chains $^{91,98}$.
The peak at $\sim$572 cm$^{-1}$ can be attributed to Mn-O lattice vibration along the chains of
MnO$_6$ octahedra$^{55}$. This band suggests the presence of the open framework of edge
sharing extended chains of MnO$_6$ and also the Mn-O stretching in the basal plane of
MnO$_6$ octahedra$^{91}$. The peak above 600 cm$^{-1}$ is due to the symmetric stretching of Mn-O
bond perpendicular to the chains of MnO$_6$ octahedra$^{91,98}$. The shifting of this band to
higher frequency region ($\sim$650 cm$^{-1}$) suggests the lowering of the number of edges shared
per MnO₆ octahedron and disruption in lattice distortion\textsuperscript{98}. Birnessite structure shares 4.8 edges per MnO₆ octahedra, however in the samples MnOx, MnOx-Y*, and MnOx-Y(Cl) they are 4 edges shared per MnO₆ octahedra characterized by shifting 600 cm\textsuperscript{-1} to higher frequency region 650 cm\textsuperscript{-1}.

The oxidation states of the manganese ions in all of the samples were examined by X-ray photoelectron spectroscopy (XPS). The manganese valence was determined by the position of the multiplet splitting of Mn 2p. The position of Mn 2p\textsubscript{3/2} has been assigned to Mn\textsuperscript{IV} (641.8-643.0 eV), Mn\textsuperscript{III} (641.4-641.9 eV), and Mn\textsuperscript{II} (640.1-641.1 eV)\textsuperscript{100-103}. The studies have shown that Mn 2p\textsubscript{3/2} spectrum of synthetic birnessite has a narrow peak maximum at 642 eV with distinct shoulder near 643 eV followed by broad shoulder between 644 and 647 eV with more contribution from Mn\textsuperscript{IV} oxidation state\textsuperscript{103}. In XPS of MnOx sample, the binding energies of Mn 2p\textsubscript{3/2} at 643.0 and 641.3 eV confirms the presence of Mn\textsuperscript{IV} and Mn\textsuperscript{III} oxidation states in the sample (Figure 24). In classical birnessite structure, there is presence of a mixture of Mn\textsuperscript{IV} and Mn\textsuperscript{III} oxidation state\textsuperscript{98}. In case of MnOx-Y(Cl) sample, the only strong binding energy of Mn 2p\textsubscript{3/2} was found at 642.5 eV confirming primary contribution from Mn\textsuperscript{IV} oxidation state (Figure 25).

Scanning electron microscopy (SEM) images showed that synthesized manganese oxides MnOx were forming cluster like structure ranging from nanosize to micronsize as shown in Figure 34 and 35. SEM images of zeolite supported manganese oxides (MnOx-Y(Cl)) showed that zeolite Y was intact (Figure 36). SEM images of MnOx-Y(Cl) showed that there was a network of nano-sized catalyst anchored on zeolite surface. The catalysts
were random sized (15-20 nm width; hard to determine the length of the sample) and well dispersed on the zeolite surface. The abundance of MnOx-Y(Cl) catalyst on the zeolite surface was high. In summary, birnessite like randomly ordered edge-sharing manganese oxides were deposited on the zeolite surface.

4.1.2 Chemical water oxidation by zeolite supported manganese oxides using CAN

Water oxidation experiment was carried out in deoxygenated aqueous solutions containing the catalyst MnOx-Y(Cl) and CAN (0.10 M, pH 0.9). The dissolved oxygen evolution kinetics of catalyst MnOx-Y(Cl) in presence of CAN is shown in Figure 47; the rate of the oxygen evolution (turn over frequency: TOF) was determined from the slope of the linear fitting of the first 100 s. The catalytic activity degraded significantly when it was reused for a consecutive oxygen evolution. The TOF of fresh MnOx-Y(Cl) in CAN was 0.96 mmol$^{-1}$mol$^{-1}$Mn$^{-1}$s$^{-1}$, and the TOF of first recovery test decreased significantly to 0.24 mmol$^{-1}$mol$^{-1}$Mn$^{-1}$s$^{-1}$. When it was reused for a second time, the TOF of the catalyst dropped to 0.16 mmol$^{-1}$mol$^{-1}$Mn$^{-1}$s$^{-1}$.

CAN has been used as a strong water oxidant because of its availability, standard chemical potential (1.75 V vs. NHE), and one-electron step process$^{73}$. The main disadvantage of CAN is its stability only under low pH condition$^{73}$. At low pH conditions, the zeolite structure starts to disrupt because of leaching of aluminum from the framework. From the XRD pattern peaks shown in Figure 9, it becomes evident that zeolite is completely destroyed after treatment with 0.10 M CAN (pH 0.9). As a result of which, the first water oxidation catalysis rate was high, but the catalysis rate dropped significantly in the second recovery. Zeolite framework was destroyed after a first run,
because of which in second run the catalysts were no longer well dispersed on the zeolite surface, ultimately reducing the accessibility of surface active sites of catalysts for water oxidation. In order to leave zeolite framework intact, pH of CAN oxidant needs to be above pH 3.0, but Ce$^{IV}$ starts to form insoluble cerium oxide materials at pH higher than 3.0. Thus for zeolite supported manganese oxides catalyst, CAN is not a suitable water oxidant.

The zeolite support is critical for this catalytic activity of the catalyst. It is necessary to prevent its destruction, which is a novel route for the synthesis of the catalyst and also it can affect the photocatalytic activity of the catalyst. Besides that, CAN water oxidant does not require light illumination and cannot be photo-generated. In order to explore artificial photosynthesis scheme, CAN oxidant cannot be practical. So we proposed to use different water oxidant other than CAN.

### 4.1.3 Photochemical water oxidation by zeolite supported manganese oxides in Ru(bpy)$_3^{2+}$-persulfate system

As an alternative to CAN, the photosensitizer ruthenium (II) tris (bipyridine) cation [Ru$^{III}$($bpy$)$_3^{3+}$] was used to study photochemical water oxidation. It is also a one-electron water oxidant with standard chemical potential (1.24 V vs. NHE)$^{73}$. The rate of oxygen evolution was studied in Ru(bpy)$_3^{2+}$- S$_2$O$_8^{2-}$ system, in which persulfate (S$_2$O$_8^{2-}$) acts as a sacrificial electron acceptor. This water oxidant is stable in slightly acidic condition (pH ~ 5)$^{73}$. This oxidant works only when irradiated with a visible light source below 560 nm resulting in the formation of relatively long lived charge-transfer excited
state Ru$^{II}$\((bpy)_3^{2+}\), and this makes it a reasonable water oxidant to study visibly light driven water oxidation\(^{25}\). Persulfate accepts the electron from excited Ru$^{II}$\((bpy)_3^{2+}\) which oxidizes to Ru$^{III}$\((bpy)_3^{3+}\). Ru$^{III}$\((bpy)_3^{3+}\) can retrieve its +2 oxidation state after it donates its hole to the catalyst, and at that site water molecules are oxidized to form oxygen molecule at the surface. It can decompose as Ru\((bpy)_3(OH)^{2+}\) in the absence of water oxidizing catalyst due to nucleophilic attack on bpy ligands eventually\(^{25}\).

There was no dissolved oxygen evolution detected with only Ru\((bpy)_3^{2+}\) and \(S_2O_8^{2-}\) in the system. There was also no photocatalytic activity of solely MnOx-Y(Cl) with the lack of either of Ru\((bpy)_3^{2+}\) or \(S_2O_8^{2-}\) in the system.

4.1.4 Buffer effect on photochemical water oxidation by zeolite supported manganese oxides

In order to improve the catalytic activity of heterogeneous catalysts for water oxidation, the choice of buffer is important. The catalytic activity of the MnOx-Y(Cl) catalyst was measured in presence of phosphate buffer (Na$_2$HPO$_4$- NaHCO$_3$, pH 7.0) and borate buffer (H$_3$BO$_3$-NaOH, pH 8.50). In phosphate buffer, the catalytic rate of MnOx-Y(Cl) was not high, but the reusability was good as shown in Figure 48 (Table 6). The TOF of the MnOx-Y(Cl) were 0.46, 0.44, and 0.36 mmol\(_{O_2}\)mol\(^{-1}\)Mn\(_s^{-1}\) in the first, second, and third run respectively. In borate buffer, the catalytic rate of MnOx-Y(Cl) were 1.75, 1.82, and 1.82 mmol\(_{O_2}\)mol\(^{-1}\)Mn\(_s^{-1}\) in the first, second, and third run respectively (Figure 49, Table 6). Though catalytic activity in presence of phosphate buffer was not as pronounced as borate buffer, the robustness of the catalyst was good in both buffer systems.
It has been reported that manganese oxides can incorporate phosphate ions, which results in the absence of di-µ-oxo bridges manganese ions and decrease in manganese oxidation state, features essential for high oxygen evolution activity. Hara et al. reported that phosphate ligand despite being a weak nucleophile, attacks the bpy rings of Ru(bpy)$_3^{2+}$ and accelerates its decomposition. It is reported that thin layer deposition of insoluble manganese phosphate occurs after adding phosphate to manganese oxide electrodes, termed a protecting coverage. The formation of phosphate suppresses the dissolution of manganese and the weak alkaline nature also depresses Mn$^{\text{III}}$ disproportionation reaction. We propose that incorporation of phosphate on the catalyst, which might block the active site of the catalyst. The XPS was carried out for the recovered MnOx-Y(Cl) sample after photochemical water oxidation in phosphate buffer as shown in Figure 32. The binding energies of Mn 2$p_{3/2}$ were at 641.0, 642.3, and 643.0 eV, the former being the most intense (Figure 32). The binding energy of P 2$p$ was at 133.2 eV (Figure 33), which confirms the presence of phosphate on the surface of the catalyst.

4.1.5 pH-dependent photochemical water oxidation by zeolite supported manganese oxides

In order to improvise the catalytic activity of MnOx-Y(Cl), borate buffer of different pH were prepared. The TOFs of MnOx-Y(Cl) in borate buffer of pH 5.0, 7.0, and 8.5 were 0.031, 0.18, and 1.75 mmol$_{\text{O}_2}$mol$^{-1}$Mn$^{-1}$s$^{-1}$ respectively (Figure 50). There was no oxygen evolution detected at pH 11.0.
It has been reported that pH of the aqueous buffer solution has a profound effect on manganese oxides stability. In acidic condition, manganese oxides are not stable and undergo dissolution. With the increase of alkalinity, there is decrement in the amount of manganese oxides dissolution as reported by Komaba et al.\textsuperscript{105} Takashima et al. also proposed that in acidic condition Mn\textsuperscript{III} valence state undergo disproportionation reaction into Mn\textsuperscript{II} and Mn\textsuperscript{IV} states; and the lack of Mn\textsuperscript{III} active site in the catalyst leads to decrease in catalytic activity.\textsuperscript{106} They showed that there is a pH-dependent activity of manganese oxides indicating Mn\textsuperscript{III} acts as precursor for water oxidation, and there is a necessity to control the disproportionation and comproportionation efficiencies for Mn\textsuperscript{III} in order to improve catalytic activity. Huynh et al. also proposed that MnOx films show high intrinsic stability in neutral and alkaline pH regime compared to acidic regime.\textsuperscript{107} The studies have reported that Mn\textsuperscript{III} has high catalytic activity because of weaker and flexible Mn\textsuperscript{III}-O bonds present in edge sharing MnO\textsubscript{6} octahedra at the surface as they are longer bonds (Jahn-Teller distortion).\textsuperscript{57,108} However, Mn\textsuperscript{IV}-O bonds are stable and less flexible.\textsuperscript{57} This might be the reason why manganese oxides catalyst did not exhibit high catalytic activity in acidic medium. With increase of alkalinity of the buffer system, Mn-O bonds at edge-sharing octahedral containing Mn\textsuperscript{III} species are present introducing a structural flexibility on the surface of manganese oxides and increases the activity for water oxidation.\textsuperscript{108}

However, when water oxidation catalysis was performed in borate buffer of pH 11.0, there was no oxygen evolution. This might be due to the fast decomposition of the photosensitizer Ru(bpy)\textsubscript{3}\textsuperscript{2+} in higher pH condition due to the nucleophilic attack of
hydroxide ion on bipyridine ring either in ground or excited state of the complex to form bpy(OH) ligand\textsuperscript{25}. Thus the optimum condition for the photochemical oxygen evolution kinetics was in borate buffer at pH 8.5 regimes.

4.1.6 Importance of high concentration of K\textsuperscript{+} ions in water oxidation catalysis

The concentration of K\textsuperscript{+} ions for water oxidation has been found important in our study. During synthesis of manganese oxides, stoichiometric concentration of potassium permanganate (0.02 M KMnO\textsubscript{4}) was used. The manganese oxides after oxidation with permanganate were named as MnOx-Y*. After precipitation of the manganese oxides on the surface of zeolite, a higher concentration of KCl (3.0 M) was used in order to remove the residual Mn\textsuperscript{2+} ions or alkaline earth metal cations from supercages of zeolite\textsuperscript{87}, and the manganese oxides was named MnOx-Y(Cl). The dissolved oxygen evolution kinetics of MnOx-Y* and MnOx-Y(Cl) were TOFs of 0.28 and 1.75 mmol\textsubscript{O2}mol\textsuperscript{-1}Mn\textsuperscript{-1} respectively (Figure 52).

The XRD reflection patterns for the sample MnOx-Y* was indicator of amorphous materials, whereas MnOx-Y(Cl) sample have XRD reflections, which resembled randomly ordered birnessite like manganese oxides. Raman spectra for both samples were similar with two strong bands at around 572 and 650 cm\textsuperscript{-1}, which suggested that there is the formation of edge sharing extended chains of MnO\textsubscript{6} octahedra layers. We observed that high concentration of K\textsuperscript{+} ions is playing an important role in improving catalytic activity of catalyst, stabilizing the structural integrity of MnO\textsubscript{2} sheets. It has been reported that higher content of K\textsuperscript{+} ions in \(\delta\)-MnO\textsubscript{2} (like birnessite) exhibits larger
catalytic activity rate per surface Mn atom as it helps in stabilizing the layered MnO$_2$ sheets compared to proton rich δ-MnO$_2$, but K$^+$ ions do not have any functional role in photolytic water oxidation catalysis$^{97}$. We also observed that precipitated MnO$_2$ layers treated with high concentration of K$^+$ ions helps to form random but ordered birnessite. Cations found in the intercalated layers of manganese oxides do not have any functional role in water oxidation catalysis, but only involved in stabilizing the layered structure of δ-MnO$_2$.$^{97}$ Dang et al reported that increase in the K$^+$ ions content in intercalated layers of manganese oxides helps in crystalline phase transformation of amorphous manganese oxides.$^{109}$ Hou et al. also reported that increase of K$^+$ ions content in octahedrally molecular sieves manganese oxides (OMS-2: MnO$_6$ octahedra forming a 2 X 2 tunnel structure) leads to increase in the catalytic activity of benzene oxidation by enhancing the activity of lattice oxygen and lowering the removal energy of lattice oxygen$^{110}$. Apart from stabilization of layered structure of manganese oxides layers, we also proposed that introduction of large amount of K$^+$ ions in precipitated MnO$_2$ might cause the exfoliation of the layered structure of manganese oxides leading to less ordered phase$^{110}$. Introduction of high concentration of K$^+$ ions in manganese oxides helps in stabilization of MnO$_2$ layers, but the defects in layered structure also enhances the catalytic activity.

**4.1.7 Role of zeolite in photochemical water oxidation**

Zeolite supported manganese oxides (MnOx-Y(Cl)) and non-supported manganese oxides (MnOx) were used to determine the dissolved oxygen evolution kinetics; and the TOFs of MnOx-Y(Cl) and MnOx were 1.75 and 0.14 mmolO$_2$mol$^{-1}$MnS$^{-1}$.
respectively (Figure 51). The catalytic activity of zeolite-supported catalyst (MnOx-Y(Cl)) was significantly higher compared to non-supported catalyst (MnOx). Both MnOx and MnOx-Y(Cl) are amorphous, poorly ordered hexagonal birnessite. Zaharieva et al. suggested that due to energetic stability of well-ordered MnO$_2$ sheets, it has low catalytic activity$^{60}$. They also suggested that well-ordered MnO$_2$ layers lacks de-protonatable groups and the lack of terminal water coordination sites for water oxidation. The distortion in the atomic structure of manganese oxides layered structure might facilitate $\mu_2$-O(H) bridging and terminal ligation of water, which increases catalytic activity. Even though both catalysts are similar structurally, the catalytic water oxidation activity of MnOx-Y(Cl) is significantly higher than MnOx. We propose that zeolite support plays an important role in enhancing the catalytic rate of manganese oxides by providing high surface area and stable dispersion of catalysts on its surface preserving the integrity of the catalytic system.

This is evident from SEM micrographs of zeolite-supported catalysts in Figure 36. The studies of improvement of catalytic activity when catalysts are dispersed on the support have been reported. Jiao et al. reported nanoscale manganese oxides clusters supported inside mesoporous silica KIT-6 as efficient and robust oxygen evolution catalysts$^{63}$. These supports help in proton management by removing protons from metal active centers and sustaining the catalytic activity of the catalyst. In manganese oxides, Mn$^{III}$ valence state has been reported to be the active metal site for water oxidation due to its structural flexibility. It is important to remove proton from metal active sites because in acidic condition manganese oxides undergo disproportionation reaction in which Mn$^{III}$
states changes to Mn$^{II}$/Mn$^{IV}$ states, which leads to degradation of the catalytic activity$^{57,108}$. We propose that zeolite channels, pores, and cages involve in proton management likewise, and protect the integrity of catalytic active metal sites of manganese oxides.

It has also been reported that spinel Co$_3$O$_4$ clusters are synthesized in nanoscale in the presence of nanostructured silica support$^7$. The high catalytic activity of Co$_3$O$_4$ is attributed to high surface area of the catalysts. A linear dependence between catalytic activities of nanoscale (5-50 nm) spinel Co$_3$O$_4$ supported on nickel foam anodes and surface area of the catalysts$^{111}$. We propose that zeolite support assist in the formation of nanoscale manganese oxides clusters on its support, increasing its surface area and ultimately its catalytic activity.

Zeolite support helps in immobilization of catalysts on its surface, which leads to more exposure of active metal sites for water oxidation catalysis. Cobalt hydroxide supported on zeolite has been studied, in which they have reported that zeolite support helps in the stabilization of catalysts and photosensitizers have an immediate access to the catalyst$^{74}$. With more dispersion of manganese oxides catalyst on the surface of zeolite, photosensitizer Ru(bpy)$_3^{2+}$ can have an easy access to the catalyst. The anionic framework of zeolite can attract positively charged photosensitizer Ru(bpy)$_3^{2+}$, and ultimately both photosensitizer and catalyst can be in a close proximity, and thus increasing the efficiency of the catalysts for water oxidation. Najafpour et al. reported nanoscale manganese oxides within faujasite zeolite as efficient water oxidizing catalyst,
but in presence of CAN water oxidant in highly acidic condition oxidant. In highly acidic regime, zeolite is not stable due to leaching of aluminum from the framework.

Zeolite-supported catalysts are in nanosize scale with high surface area. Despite the high loading of manganese in non-supported manganese oxides MnOx, the dissolved oxygen evolution kinetics per Mn active center was low compared to zeolite supported manganese oxides MnOx-Y(Cl). The higher catalytic activity for these zeolite supported catalysts (MnOx-Y(Cl)) can attributed to high surface areas of nanoclusters of manganese oxides deposited on zeolite surface as well as good dispersion of these catalysts on the support.

4.2 Influence of alkaline earth metal cations in zeolite-supported manganese oxides in photochemical water oxidation

In Photosystem II (PS II), the oxygen-evolving center has been known to be calcium manganese cluster (CaMn₄O₅)₁¹. Inspired from PS II system, we proposed to use alkaline earth metal cations doped manganese oxides and study its catalytic activity. We synthesized zeolite- supported alkaline earth metal cations doped manganese oxides using Mg²⁺ doped (MgMnOx-Y(Cl)), Ca²⁺ doped (CaMnOx-Y(Cl)), Sr²⁺ doped (SrMnOx-Y(Cl)), and Ba²⁺ doped (BaMnOx-Y(Cl)).

4.2.1 Structural characterization of zeolite-supported alkaline earth metal cations doped manganese oxides

The XRD reflection patterns of MgMnOx-Y (Cl), CaMnOx-Y(Cl), SrMnOx-Y(Cl), and BaMnOx-Y(Cl) were similar to that of MnOx-Y(Cl). The XRD broad peaks
were observed at \( \theta \approx 12.5^\circ \) (7 Å), 24° (3.5 Å), and 36° (2.5 Å) as shown in Figure 14, 15, and 16. These reflections suggested to be amorphous, poorly ordered hexagonal birnessite like manganese oxides similar to undoped manganese oxides (MnOx-Y (Cl))\(^{92,96}\). HR-TEM images of SrMnOx-Y(Cl) and BaMnOx-Y(Cl) showed that these catalysts are crystalline phases (2.5 Å and 3.5 Å lattice spacing), but a lattice spacing corresponding to the diffraction pattern at 12.5° could not be detected (Figure 44, 45). Raman scattering for these samples showed the effect of cations on these manganese oxides structure as shown in Figure 22. All samples possessed a strong band at ~572 cm\(^{-1}\), which suggested that alkaline metal cations doped manganese oxides possess the Mn-O lattice vibration as expected for manganese oxides\(^{91}\). These catalysts possess edge sharing extended chains of MnO\(_6\) octahedra similar to MnOx-Y(Cl). A band at ~650 cm\(^{-1}\) of these alkaline earth metal cations doped manganese oxides differed in relative intensity compared to ~572 cm\(^{-1}\) band depending on the type of alkaline earth metal cations. The manganese oxides depend on the arrangement of MnO\(_6\) octahedral units in terms of number of extended chains and tunnel openings\(^{91,98}\). From the Raman scattering, we observed that MgMnOx-Y(Cl), CaMnOx-Y(Cl), and SrMnOx-Y(Cl) samples have two frequencies that matches the birnessite structure where intercalated layers of MnO\(_6\) octahedral chains are filled with respective di-valent cations Mg\(^{2+}\), Ca\(^{2+}\), and Sr\(^{2+}\) along with K\(^+\) ions and water molecules to balance the anionic vacancies of manganese oxides layers. It also has crystal symmetry of hexagonal with (1 X ∞) tunnel layers with an average of 4 shared edges per MnO\(_6\) octahedron similar to MnOx-Y(Cl) (Cl). The band at ~650 cm\(^{-1}\) has lower intensity relative to ~572 cm\(^{-1}\), and this attenuation is observed when
heavy ions decrease the Mn-O lattice vibration perpendicular to the octahedral chains of manganese oxides\textsuperscript{91}. In case of BaMnOx-Y(Cl) sample, this high frequency band looked intense when compared to ~572 cm\textsuperscript{-1} band, suggesting that heavier doped cations in manganese oxides, the more damping of MnO\textsubscript{6} vibrational components along the octahedral chains. The barium ions doped manganese oxides have been studied, and its Raman spectrum matches to romanechite with large tunnel openings generated by triple chains of MnO\textsubscript{6} octahedra containing Ba\textsuperscript{2+} ions\textsuperscript{88,91,112}. Ba\textsuperscript{2+} ions are found to be the major cation in the tunnel of romanechite\textsuperscript{113,114}. Doping of different types of alkaline earth metals cations on manganese oxides do not have that significant impact on Mn-O lattice vibration of MnO\textsubscript{6} octahedral chains of birnessite like manganese oxides except for large cations like Ba\textsuperscript{2+} ions.

The XPS studies showed that the alkaline earth metal cations doped manganese oxides contain Mn\textsuperscript{IV} and Mn\textsuperscript{II} valence states on the surface of the catalyst (Table 4). Referring to valence states of manganese in these catalysts, the studies show that manganese oxides match to birnessite. Birnessite have the high concentration of Mn\textsuperscript{IV} with a tetravalent negative charge is present at every cation vacancy. With hydrated alkaline earth metal cations and potassium ions, triple corner sharing Mn\textsuperscript{III} octahedral sites exist in the interlayer, and water molecules counterbalance these cationic vacancies. SEM images of alkaline earth metal cations doped manganese oxides showed that those manganese oxides are deposited on the surface of zeolite. HR-TEM images also showed that these catalysts are anchored on the zeolite support (Figure 44, 45). The abundance of catalysts on the surface of zeolite followed the trend: MgMnOx-Y(Cl) > CaMnOx-
Y(Cl)~ SrMnOx-Y(Cl) >> BaMnOx-Y(Cl) (Figures 37-40 respectively). The catalysts were in nanoscale range (length: 80-100 nm; diameter: 15-20 nm) network like catalysts encompassing the zeolite surface. Among four catalysts, BaMnOx-Y(Cl) sample had lower amount of catalysts on zeolite surface. EDX analysis also confirmed the presence of barium and manganese on the zeolite (Figure 46).

From elemental analysis (atomic absorption spectroscopy (AAS)), Mn loading in each sample was measured (refer to Table 2) which showed the Mn loading inside zeolite depends on the cationic size of alkaline earth metals. The Mn loading on the zeolite supported manganese oxides had the following order: MgMnOx-Y(Cl) > CaMnOx-Y(Cl) ≥ SrMnOx-Y(Cl) > BaMnOx-Y(Cl) (5.4%, 2.7%, 2.2%, and 1.2% Mn wt/wt% respectively). These Mn loading results are also evident from the observation of SEM images. With the increase in cationic size of alkaline earth metals cations, the Mn loading inside the zeolite supercages decreases. During ion exchanging of alkaline earth metal cations and manganese ions in zeolite, these ions compete with each other. Since Ba$^{2+}$ cation is the largest among the divalent alkaline earth metal cations, it competes more and retards the ion exchanging of Mn$^{2+}$ ions inside the zeolite supercages. The color of the catalyst of manganese oxides supported on zeolite had different shades of brown depending upon the alkaline earth metal cations doped. The color of MnOx-Y(Cl) was dark brown, whereas in case of alkaline earth metal cations doped manganese oxides the shades of brown got lighter in the following order: BaMnOx-Y(Cl) > SrMnOx-Y(Cl)~CaMnOx-Y(Cl) > MgMnOx-Y(Cl). The lighter the color of the catalyst, the lower the loading of Mn inside the zeolite during ion exchange. This trend also basically
showed that as the size of cations increases, Mn loading on zeolite decreases, and so does the amount of manganese oxides deposition on zeolite surface.

4.2.1 Photochemical water oxidation by zeolite supported alkaline earth metal cations doped manganese oxides

The photochemical water oxidation for all alkaline earth metal cations doped manganese oxides was better than manganese oxides MnOx-Y(Cl) itself except for MgMnOx-Y(Cl) when normalized to Mn content of the catalyst as shown in Figure 53. Alkaline earth metal cations seem to influence the catalytic activity of manganese oxides. Determining the role of alkaline cations whether structural or functional in the catalytic activity is hard to elucidate. We propose that doping of alkaline cations in manganese oxides helps in stabilization of the layered structure of manganese oxides, which ultimately enhances its catalytic activity of water oxidation.

Many studies have been done with different polymorphs of manganese oxides and calcium manganese oxides. Zaharieva et al. examined calcium-manganese oxides, and proposed a Ca$^{2+}$ role similar in PSII functionally and structurally. They proposed that mixed valence state of manganese oxides between +3 and +4, poorly stacked layered structure, and connection of Ca$^{2+}$ ions by oxo-bridges helped to enhance the catalytic activity. Webb et al. proposed that Ca$^{2+}$ ions present in between the MnO$_2$ layers helped to stabilize birnessite structure as well as it increases the rate of formation of birnessite. Drits et al. also suggested that Ca$^{2+}$ ions between interlayer of MnO$_2$ sheets helps in control the stacking of Mn$^{3+}$-sheets but still they are poorly basal stacked. Structural
defects and poor stacking of chains of MnO$_6$ octahedra were observed in our synthesized alkaline manganese oxides, and is correlated with efficient water oxidizing activity.

Wiechen et al. studied the influence of alkaline earth metal cations Mg$^{2+}$, Ca$^{2+}$, and Sr$^{2+}$ in the catalytic activity of layered manganese oxides$^{71}$, and the trend of catalytic activity was in the following trend: Mg$^{2+}$$<<$ Sr$^{2+}$$<$ Ca$^{2+}$. They proposed that the presence of bridging oxido or terminal oxy groups, hydroxides are essential for O-O bond formation and similar to OEC of PSII. They adopted the mechanistic aspect of oxygen evolution of PSII in order to explain the role of Ca$^{2+}$ in their catalyst. However, the mechanistic aspect of OEC in PSII is in bio-homogeneous system, and it is unreliable to compare its mechanistic aspect as well as its catalytic activity to heterogeneous system. There should be a possible structure-function relationship of heterogeneous catalysts that can explain the trend of different alkaline earth metal cations doped manganese oxides. The trend of catalytic activity of alkaline earth metal cations doped manganese oxides supported on zeolite was observed in the following order: BaMnOx-Y(Cl)> SrMnOx-Y(Cl)> CaMnOx-Y(Cl)> MgMnOx-Y(Cl) as shown in Figure 53. The dissolved oxygen evolution TOFs of BaMnOx-Y(Cl), SrMnOx-Y(Cl), CaMnOx-Y(Cl), and MgMnOx-Y(Cl) were 7.12, 4.10, 2.90, and 1.43 mmol$_{O_2}$mol$^{-1}$Mn$^{-1}$s$^{-1}$ respectively (Figure 53). Barium cation doped manganese oxides (BaMnOx-Y(Cl)) was the most active catalyst for water oxidation.

We observed that catalytic performances of catalyst get better with the increasing size of alkaline earth metal cations. From SEM images shows the abundance and size of the catalysts deposited on the zeolite surface are different. The smallest size cation Mg$^{2+}$ doped manganese oxide, MgMnOx-Y(Cl) sample, has the largest size and high
and the largest size cation Ba$^{2+}$ doped manganese oxide, BaMnOx-Y(Cl) sample, has the smallest size and low abundance of particles. Nanoscale particles have high surface to volume ratio, which results in high surface area. An exponential increase in the percentage of atoms localized on the surface of nanoparticles with decrease in nanoparticle diameter has been shown$^{116}$. Since only surface sites of catalyst are accessible to photosensitizer Ru(bpy)$_3$$^{2+}$ complex, high surface area and particle size play an important role in this catalysis. Since BaMnOx-Y(Cl) catalyst has the smallest nanoscale cluster anchored on the zeolitic surface, it has more active Mn centers exposed on the surface increasing its accessibility to photosensitizer. Fekete et al. also reported that their catalyst MnO$_2$ films have higher activity due to smaller particle size and higher surface area$^{117}$. Risch et al. also reported that the redox-inert cations are not involved in the elementary, rate-determining step in water oxidation$^{90}$. They also reported that water oxidation catalytic activity of their cobalt-oxido clusters decreases with increasing cluster sizes. The results of high catalytic water oxidation by BaMnOx-Y(Cl) were reproducible with an average TOF of 6.75 ± 0.69 mmol$_2$mol$^{-1}$Mn$^{-1}$s$^{-1}$ as shown in Figure 54 (refer to Table 11).

Apart from particle size and high surface area of the catalysts, high catalytic activity of zeolite supported manganese oxides is related to its structure. The synthesized catalysts are amorphous and analogous to poorly ordered birnessite like layered manganese oxides with cation vacancies in the MnO$_2$ sheets. Presence of cation vacancies can be influential in catalytic activity due to presence of unsaturated oxygens that protons can bind to. It has been reported that $\mu$-OH can undergo deprotonation and
help in proton coupled electron transfer during water oxidation catalysis. We propose that when large sized cations like \( \text{Ba}^{2+} \) are doped into manganese oxides, it leads to more exfoliation of the layered manganese oxides sheets increasing its surface area for more sites for the coordination of water to the catalyst surface.

The dissolved oxygen measurement showed saturation within 5 minutes. The amount of dissolved oxygen evolved for the best sample \( \text{BaMnOx-Y(Cl)} \) was \( \sim 14 \) \( \mu \text{mol} \) (\( \sim 1000 \text{mmol}_2\text{mol}_\text{Mn}^{-1} \)), which was less than expected stoichiometric amounts of dissolved \( \text{O}_2 \) evolution (total possible oxygen based on the amount of persulfate: \( \sim 800 \) \( \mu \text{mol} \); in air-saturated solution: \( \sim 19 \) \( \mu \text{mol} \)) based on the amount of persulfate (Figure 53). GC was used to measure the amount of gas-phased oxygen evolution by the best catalyst \( \text{BaMnOx-Y(Cl)} \) as shown in Figure 55. In our work, the total amount of oxygen that can be generated based on the concentration of \( \text{S}_2\text{O}_8^{2-} \) was about \( 400 \) \( \mu \text{mol} \), but the amount of gas-phased oxygen evolved at steady state was \( \sim 75 \) \( \mu \text{mol} \) in about an hour of reaction. Jiao et al. reported that total amount of gas-phased oxygen evolved at steady state was \( \sim 145 \) \( \mu \text{mol} \), and the expected stoichiometric amount of oxygen evolution was \( \sim 275 \) \( \mu \text{mol} \). Amorphous manganese oxides are reported to have the total amount of dissolved oxygen about \( \sim 70 \) \( \mu \text{mol} \) (expected amount of oxygen: \( \sim 400 \) \( \mu \text{mol} \)) under photochemical \( \text{Ru(bpy)}_3^{2+} \)-persulfate condition measured by GC. Solution-phase and gas-phase \( \text{O}_2 \) measurements usually show saturation within minutes of photolysis, before the stoichiometric amounts of \( \text{O}_2 \) are generated. This observation might be due to decrease in the concentration of photosensitizer \( \text{Ru(bpy)}_3^{2+} \) in the solution resulted from photodecomposition. \( \text{Ru(bpy)}_3^{2+} \) are stable and works efficiently in mildly acidic
condition (pH~5). In alkaline condition (above pH~5), bpy ligands of Ru(bpy)$_3^{2+}$ are susceptible to nucleophilic attack by OH$^-$ ligand causing fast photodegradation. The concentration of Ru(bpy)$_3^{2+}$ was measured by monitoring MLCT absorption band in the range of 400-500 nm, which decreased significantly after photolysis in alkaline borate buffer (pH 8.5) as shown in Figure 57. This photodegradation of Ru(bpy)$_3^{2+}$ becomes kinetically competitive with oxygen evolution, as a result of which water oxidation ceases to carry on after few minutes of photolysis.

### 4.2.3 Comparison with other manganese oxides catalysts from literature

Manganese oxides catalysts reported in the literature were also investigated and summarized in Table 12. These are dissolved oxygen measurement in photochemical Ru(bpy)$_3^{2+}$-S$_2$O$_8^{2-}$ system. Compared to reported catalysts, BaMnOx-Y(Cl) catalyst has the highest catalytic rate for water oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (mmol O$_2$ mol$^{-1}$ MnS$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaMnOx-Y(Cl)</td>
<td>7.21</td>
<td>This work</td>
</tr>
<tr>
<td>MnOx</td>
<td>0.14</td>
<td>This work</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>1.90</td>
<td>108</td>
</tr>
<tr>
<td>Amorphous manganese oxides (AMO)</td>
<td>0.046</td>
<td>55</td>
</tr>
<tr>
<td>KIT-6 mesoporous silica/Mn clusters</td>
<td>0.212</td>
<td>63</td>
</tr>
<tr>
<td>α-MnO$_2$ nanowires</td>
<td>0.059</td>
<td>54</td>
</tr>
<tr>
<td>Bulk α- MnO$_2$</td>
<td>0.010</td>
<td>54</td>
</tr>
<tr>
<td>β-MnO$_2$</td>
<td>0.020</td>
<td>54</td>
</tr>
<tr>
<td>CaMn$_3$O$_6$</td>
<td>0.002</td>
<td>67</td>
</tr>
<tr>
<td>CaMn$_2$O$_4$.H$_2$O</td>
<td>0.350</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 12: Literature report of catalytic rate of manganese oxides water oxidizing catalyst.
4.3 Influence of anions in zeolite-supported alkaline earth metal cations doped manganese oxides in photochemical water oxidation

After oxidation of Mn\textsuperscript{II} by KMnO\textsubscript{4}, the precipitation of manganese oxides occurs on the surface of zeolite. In order to remove the residual Mn\textsuperscript{2+} ions and other cations from zeolite cage, high concentration of KCl was used. In place of KCl, KOH and KNO\textsubscript{3} were used to remove those residual cations. Since barium cation doped manganese oxides was the most active water oxidizing catalyst, zeolite supported Ba\textsuperscript{2+} ions doped manganese oxides was synthesized using KCl, KNO\textsubscript{3}, and KOH (BaMnO\textsubscript{x}-Y(Cl), BaMnO\textsubscript{x}-Y(NO\textsubscript{3}), and BaMnO\textsubscript{x}-Y (OH) respectively).

4.3.1 Structural characteristics of zeolite supported alkaline earth metal cations doped manganese oxides treated with different anions

The XRD reflection patterns of BaMnO\textsubscript{x}-Y(Cl) and BaMnO\textsubscript{x}-Y(NO\textsubscript{3}) were similar to that of MnO\textsubscript{x}-Y(Cl). The XRD broad peaks were observed at $2\theta \sim 12.5^\circ$ (7\textdegree\text{ Å}), 24\textdegree (3.5 \text{ Å}), and 36\textdegree (2.5 \text{ Å}) as shown in Figures 17, 18, and 19 suggesting amorphous, poorly ordered birnessite like manganese oxides. The peaks at 24\textdegree (3.5 \text{ Å}), and 36\textdegree (2.5 \text{ Å}) were even less intense and broadened in BaMnO\textsubscript{x}-Y (OH) sample, and this suggested even more disordered amorphous manganese oxides. The characteristic XRD peak at 12.5\textdegree (7\textdegree\text{ Å}) was also not observed in BaMnO\textsubscript{x}-Y (OH) as shown in Figure 17. Raman scattering patterns showed the major structural differences among these catalysts as shown in Figure 23. As stated earlier, BaMnO\textsubscript{x}-Y(Cl) has an intense band at 572 cm\textsuperscript{-1} and intense 650 cm\textsuperscript{-1} band, which matches to romanechite structure of manganese
oxides. BaMnOx-Y(NO₃) sample had both strong bands at 572 and 650 cm⁻¹, where the latter band was less intense compared to the former band matching to birnessite like manganese oxides. In case of BaMnOx-Y (OH), both bands were destroyed and less intense, and this also suggests that edge-sharing MnO₆ octahedral extended chains were disturbed. Raman spectra suggest that these anions affect the Mn-O lattice vibration of MnO₆ octahedral chains, having redox-inert K⁺ ions in all cases. XPS results showed that BaMnOx-Y (OH) contains Mn⁴⁺ valence state, and BaMnOx-Y(NO₃) contained both Mn⁴⁺ and Mn²⁺ valence state similar to BaMnOx-Y(Cl) as shown in Figure 30 and 31 respectively. SEM images confirmed that treatment with different anions does not induce any difference to morphological structures of manganese oxides deposited on the zeolite surface as shown in Figure 41 (BaMnOx-Y(NO₃)) and Figure 42 (BaMnOx-Y(OH)).

4.3.2 Influence of anions on photochemical water oxidation by zeolite-supported alkaline earth metal cations doped manganese oxides

The dissolved oxygen evolution kinetics for BaMnOx-Y(Cl), BaMnOx-Y(NO₃), and BaMnOx-Y (OH) was measured to be 7.21, 5.93, and 4.67 mmolO₂mol⁻¹Mn⁻¹s⁻¹ as shown in Figure 38. The highest catalytic activity was found for BaMnOx-Y(Cl), whereas BaMnOx-Y (OH) has the low catalytic rate of water oxidation. The results show that there should be structural-functional relationships in these catalysts. Risch et al. reported that anion type of the electrolyte affect the order and size of cobalt oxide clusters used for water oxidation as well as modulate the redox chemistry of their catalyst. Cheney et al. reported the effect of Hoffmeister anions on nanostructures of birnessite
and cryptomelane, produced by the reduction reaction of potassium permanganate and manganese sulfate in acidic media, have been studied\textsuperscript{119}. They reported these hoffmeister anions like Cl\textsuperscript{-} ions affect the structure and morphology of birnessite manganese oxides nanostructures. But in our case, different types of anions were used after manganese oxides were synthesized after permanganate reduction.

The structural characterization of these catalysts show that with the treatment of KOH leads to the disruption of layered structure of manganese oxides, and this can be the reason for decrease in the catalytic activity. Raman scattering of these catalysts show the anions do effect the crystal structure as well as ordering of MnO\textsubscript{6} octahedral extended chains, where both Mn-O lattice vibration parallel and perpendicular to MnO\textsubscript{6} octahedral chains were dampened. This might lead to decreasing accessible active sites such as di-\(\mu\)-oxo-bridges metal ions for water oxidation. Further in-situ investigations are required to elucidate the structure-functional impact of these anions on structure of manganese oxides and to understand the chemistry of water oxidation in zeolite supported manganese oxides.
4.4 Conclusion

Nanostructured manganese oxide clusters were successfully deposited on the surface of the zeolite Y support by ion exchanging followed by precipitation of manganese oxides. Two different manganese oxide clusters were synthesized: manganese oxides and alkaline earth metal cations doped manganese oxides. Non-supported manganese oxide catalysts were also synthesized. Different characterization techniques were used in order to determine the composition of the catalyst. XRD patterns revealed that both zeolite supported manganese oxides and alkaline earth metal cations doped manganese oxides are poor crystalline with birnessite like layered structure of MnO$_6$ octahedral chains. Raman scattering studies showed that the catalysts are edge sharing MnO$_6$ octahedra with birnessite like structure. XPS showed that manganese oxides catalysts have Mn$^{3+}$/Mn$^{4+}$ oxidation states, which match to AOS of manganese in birnessite, which have cationic vacancies, counterbalanced by alkali cations. It also showed that large amount of K$^+$ ions are present in the manganese oxides structure. SEM micrographs showed that nanoscaled manganese oxides clusters are deposited on the support zeolite Y which are nanosized ranging from 40-70 nm. HRTEM showed that the catalysts have crystalline phases of basal spacings of MnO$_2$ sheets. All these characterization showed that the catalyst on the surface of zeolite is poorly ordered edge sharing MnO$_6$ octahedra birnessite like structure.

Photochemical water oxidation tests in presence of Ru(bpy)$_3^{2+}$-S$_2$O$_8^{2-}$ system were carried out for different catalysts in presence of high alkalinity of borate buffer.
Zeolite supported manganese oxides were found to be more active water oxidizing catalysts than non-supported manganese oxides. We propose that zeolite support provides stability to the catalyst, good dispersion of catalysts leading to more exposure of Mn active sites for water oxidation. Zeolitic anionic framework brings positively charged water oxidant Ru(bpy)$_3^{2+}$ in close proximity to the catalyst assisting efficient water oxidation. We also propose that zeolite support also has role in proton management through proton transfer through its cavities and pore channels. The catalytic activity of zeolite supported alkaline earth metal cations doped manganese oxides (NMnOx-Y(Cl); N: alkaline earth metals Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) and zeolite supported manganese oxides (MnOx-Y(Cl)) were compared, and it showed that NMnOx-Y(Cl) catalysts were more active catalyst than MnOx-Y(Cl). We proposed that alkaline earth metals helps in the stacking of Mn oxides layers and provides more structural stability. When comparing the catalytic activities of alkaline earth metal cations, the following trend was observed: Mg$^{2+} < $ Ca$^{2+} < $ Sr$^{2+} < $ Ba$^{2+}$. The catalytic rate of dissolved oxygen evolution increased as the cationic size of the alkaline earth metal cations increased. From SEM micrographs, we can see that abundance and size of the catalysts increases with the decrease in the cationic size of alkaline earth metals. We propose that with the increase in cationic size of alkaline earth metals which are being ion exchanged simultaneously with Mn$^{2+}$ ions, the manganese loading decreases, and which ultimately leads to the decrease in size of nanocluster on the surface of zeolite Y. With the decrease in the size of the catalysts, it increases the surface area of the catalyst, which exposes more active sites for water oxidation.
In summary, zeolite supported manganese oxides catalyst with alkaline earth metals with largest cation size is found to be the best catalyst for water oxidation. Since the synthesis of the catalyst on zeolite surface has been successful, the synthesis of this catalyst deposited on the zeolite membrane looks promising. In future, these manganese oxides clusters deposited on the surface of zeolite membrane will be synthesized and its photochemical water oxidation tests will be carried out.
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\[(\text{H}_2\text{O})(\text{terpy})\text{Mn(\text{\(\mu\)-O}\text{)}_2}\text{Mn(terpy)}(\text{OH}_2))(\text{NO}_3)_3(\text{terpy} = 2,2':6,2''-\text{terpyridine})\]

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