V.N.17 Porous Transition Metal Oxides: Synthesis, Characterization, and Catalytic Activity

Principal Investigator: Steven L. Suib

The University of Connecticut
Unit 3060, Depts. of Chemistry and Chemical Engineering
55 N. Eagleville Rd., University of Connecticut,
Storrs, CT 06269-3060
Phone: (860) 486-2797
Email: Steven.Suib@uconn.edu

Names of Team Members:
Altug Poyraz, Chung Hao Kuo, Saminda Dharmarathna,
The University of Connecticut
Unit 3060, Depts. of Chemistry
55 N. Eagleville Rd., University of Connecticut
Storrs, CT 06269-3060
Phone: (860) 486-2797
Email: Altug.Poyraz@uconn.edu,
ChungHao.Kuo.Suib@uconn.edu,
Saminda Dharmarathna@uconn.edu

DOE Program Manager: Dr. Raul Miranda
Phone: (301) 903-8014
Email: Raul.Miranda@science.doe.gov

Objectives

The goals of this project are as follows:

a. To synthesize well ordered crystalline mesoporous transition metal oxide (MTMO) materials with monomodal uniform pore sizes.

b. To prepare and characterize ordered mesoporous thin films.

c. To optimize catalytic activity, selectivity, and stability in oxidation catalysis using amorphous porous oxides and crystalline microporous and mesoporous materials.

d. To investigate the role of mesoporous materials in battery systems.

e. To develop novel *in situ* characterization methods for syntheses, selective oxidations, and battery studies.

Technical Barriers

The technical barriers in this project include synthesis of catalysts and obtaining excellent catalytic yields and stabilities. The synthesis barriers are related to the generic preparation of metal and nonmetal oxide mesoporous systems. Some materials are more difficult to make than others. Right now some are not able to be made. The catalysis barriers involve optimizing the pore size of the catalysts, optimizing active sites, and understanding factors that give stability to the systems.

Abstract

This project concerns the synthesis of well-ordered crystalline mesoporous transition metal oxide (MTMO) materials with monomodal uniform pore sizes. Characterization of the physical and chemical properties of these materials is being done with a variety of methods. Several catalytic reactions are being studied such as photo-assisted catalytic water splitting, catalytic coupling of diamine and hydroxyketones, quinoxaline formation, selective catalytic oxidation of adamantane, and three component coupling Hantzsch reactions. In addition, such materials are being studied in battery applications.

Progress Report

Sub Topic 1: Synthesis of Mesoporous Materials.

Research in the area of synthesis of microporous and mesoporous materials is ongoing.[1-20] Unique University of Connecticut (UCT) type metal oxide materials have been prepared that have crystalline walls, monomodal mesopore size distributions, and high thermal stabilities. These materials are under development through a licensing agreement. In addition, several microporous materials have been prepared that are being studied in a variety of catalytic reactions like photo-assisted catalytic oxidation of water[7,14] and several selective and total oxidation reactions.[4-6,8,11,15,19] Activities of these systems are often controlled by the amount of defects, especially oxygen ion vacancies, as well as dopants. Another emphasis has been on the activation of CO_2 to produce useful chemicals and fuels by electrochemical methods.[10,16-17,20] Another active area has been studies of metal oxide and mixed metal oxides with the control of particle size and morphology and their influence on catalytic properties.[1,5,9,11,12]

Sub Topic 2: Photoassisted Water Splitting with Porous Metal Oxides.

Water oxidation is the bottleneck in artificial photosynthetic systems that aim to split water into hydrogen and oxygen. However, water oxidation occurs readily in plants, catalyzed by the Mn_4O_4Ca manganese cluster. Manganese minerals are ubiquitous in nature displaying layered and tunnel structures. In our studies,[7,14] mixed valent porous amorphous manganese oxides (AMO), along with cryptomelane type tunnel manganese oxides (OMS-2) and layered birnessite (OL-1) have been used as water oxidation

catalysts. Significantly higher turnovers were obtained with AMO (290 mmol O_2/mol Mn) compared to tunnel structure OMS-2 (110 mmol O_2/mol Mn) and layered structure OL-1 (27 mmol O_2/mol Mn) in water oxidation tests with Ce^{4+}. Oxygen evolution was also confirmed under photochemical conditions using $[Ru(bpy)_3]^{2+}$ as a photosensitizer and persulfate as a sacrificial agent. The differences in catalytic activity among these catalysts have been probed using X-ray diffraction, transmission electron microscopy, Raman and Fourier transform infrared (FTIR) spectroscopy, average oxidation state, and compositional analyses. Comparison of AMO against prominent manganese catalysts described in literature shows AMO provided the highest turnover numbers. AMO catalyst was also reusable after regeneration. O-18 labeling studies proved that water was the source of dioxygen and IR proved the structural stability of AMO after reaction. AMO is related to hexagonal birnessites such as layered biogenic manganese oxides or H^+-birnessite that have cation vacancies in the MnO_2 sheets rather than completely filled Mn^{3+}/Mn^{4+} sheets, and this is influential in catalytic activity. A reaction scheme, scanning electron micrograph of the best photocatalyst, and proposed structure is given in **Figure 1**.

Sub Topic Hydrocarbon Oxidations.

A representative study of catalytic oxidations involves the bi-modification *in situ* oxidation at interfaces (IOI) coupled with an ion-exchange synthesis method that has produced mesoporous silicon oxide (MPS) templates. Manganese oxide was formed at the internal surface of the MPS template by IOI. In this IOI method, high valent oxo-anions of Mn (MnO_4^-) were used for the selective oxidation of polyethyleneoxide (PEO) groups of Pluronic ($PEO_{20}PPO_{70}PEO_{20}$) surfactant and formed manganese oxide at the organic-inorganic (corona) interface. The oxide formation was restricted at the corona interface by a positively charged CTA^+ head group of the cationic surfactant CTABr. The second modification of the MPS template was done by introducing promoter ions (Cs^+, K^+) or H^+ by an ion-exchange reaction between CTA^+ and the ions. The bi-modified MPS-Mn-X (X = Cs, K, or H) samples preserved the mesoporosity and high surface area of the MPS template. The bi-modified MPS-Mn-X samples were found to be more
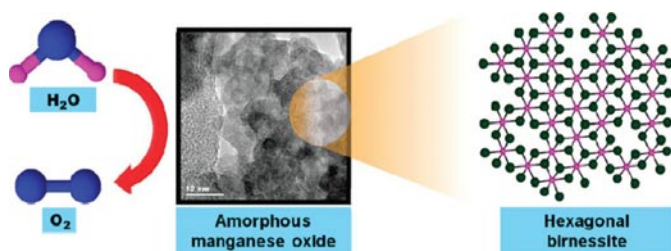
active, selective, and stable than the singly modified MPS-Mn sample for gas phase oxidation of toluene.

This study illustrates the synthesis, characterization and catalytic performance of the bi-modified mesoporous silicon oxides (MPS-Mn-X where X= Cs, K, or H). First, manganese oxide clusters were formed and kept at the positively charged organic-inorganic interface of the as-synthesized mesoporous silicon oxide by the "*in-situ* oxidation at interface" method. Unlike traditional wet- impregnation methods, the newly developed method restricts manganese oxide formation in the mesopore structure and uses as-synthesized mesoporous templates rather than calcined ones. The second modification was then carried out using the singly modified MPS-Mn sample and introducing promoter cations (K^+ and Cs^+) or H^+ using ion-exchange reactions between the cations and CTA^+. The synthesized bi-modified MPS-Mn-X preserved the advantages of the MPS template such as having highly ordered mesopore structures, high surface areas, and regular-cylindrical mesopores. The synthesized bi-modified MPS-Mn-X samples were tested for catalytic total oxidation of toluene under oxygen deficient conditions. The bi-modified MPS-Mn-X catalysts exhibited higher performance, selectivity, and stability compared to the singly modified MPS-Mn catalysts. The higher performance of the bi-modified MPS-Mn-X catalysts in catalytic oxidation of toluene (**Figure 2**) is attributed to creation of more active Mn^{3+} sites on the catalyst surfaces by the promoter ions.

A different strategy to create selective oxidation catalyst has involved use of ultrasonic cavitation in the synthesis of
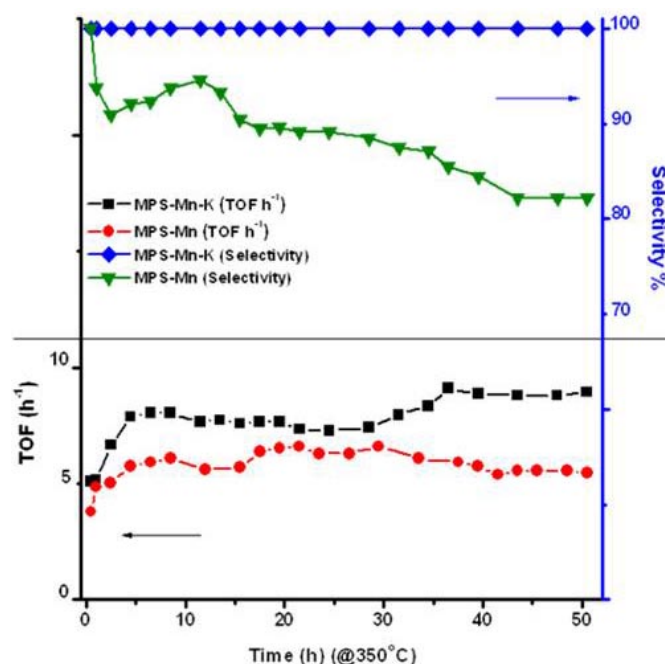

FIGURE 1. Photoassisted Catalytic Water Splitting, Scanning Electron Micrograph, and Proposed structure of the Active Catalyst.

FIGURE 2. 50 h stability test TOF (h-1) and % CO2 selectivity results for MPS-Mn and MPS-Mn-K catalysts.

novel materials. A rapid, direct sonochemical method was successfully developed to synthesize cryptomelane-type manganese octahedral molecular sieve (OMS-2) materials. Very high surface area of 288 ± 1 m^2/g and small particle sizes in the range of 1−7 nm were produced under nonthermal conditions. No further processing such as calcination was needed to obtain the pure cryptomelane phase. A co-solvent system was utilized to reduce the reaction time and to obtain higher surface areas. Reaction time was reduced by 50% using water/acetone mixed phase solvent systems. The cryptomelane phase was obtained with 5% acetone after 2 h of sonication at ambient temperature. Reaction time, temperature, and acetone concentration were identified as the most important parameters in the formation of the pure cryptomelane phase. OMS materials synthesized using the above-mentioned method were characterized by X-ray diffraction, nitrogen sorption, scanning electron microscopy, transmission electron microscopy, and Fourier transformation infrared spectroscopy. OMS-2 materials synthesized using sonochemical methods possess greater amounts of defects and hence show excellent catalytic performances for oxidation of benzyl alcohol as compared to OMS-2 synthesized using reflux methods and commercial MnO$_2$. Surface areas and particle sizes are shown in Table 1. Table 2 shows some of the catalytic results for selective oxidation of toluene.

Future Directions

Future directions of this project include synthesis of new mesoporous materials that are difficult to make including some transition metal systems, nonmetal oxide systems, mixed metal systems, and doped Mesoporous materials. Characterization studies include determination of fundamental properties of these systems and using such information as feedback to the syntheses to make better materials as regards purity, controlled structures, and controlled compositions. Catalytic studies will involve optimization of selectivities and activities in the reactions described above.

TABLE 1. BET Surface Area of As Synthesized OMS-SC Samples[a]

OMS-sc Sample	BET s.a. ± 1 (m^2/g)	particle size (nm)	OMS-sc Sample	BET s.a. ± 1 (m^2/g)	particle size (nm)
4 h	245	2.8	10% ACE - 2 h	188	3.3
8 h	115	6.1	10% ACE - 3 h	199	2.7
12 h	118	5.4	10% THF - 3 h	200	1.0
3 h −55 °C	267	2.4	10% DMSO - 3 h	246	3.2
3 h −65 °C	177	6.6	10% DEE - 3 h	250	2.2
			10% SULF. - 3 h	286	4.2
K-OMS-2$_{REF}$	88	11.4	10% TOLU. - 3 h	288	5.4

[a]THF, tetrahydrofuran; DMSO, dimethylsulfoxide; DEE, diethyl ether; ACE, acetone; SULF., sulfolane; TOLU., toluene.

TABLE 2. Selective Oxidation of Benzyl Alcohol[a]

catalyst	BET s.a. ± 1 (m^2/g)	Conv. %[b]	Sel. %[c]	TON[d]
K-OMS-2$_{SC-10\%Tolu.}$	288	52 (28[e])	100	8.32
1st recovery[f]		36 (39[h])	100	7.58
2nd recovery[g]		18 (20[h])	100	7.2
K-OMS-2$_{SC-12h}$	118	39	100	6.24
K-OMS-2$_{REF}$	88	21	100	3.36
commercial MnO$_2$	28	15	100	2.4

[a]Reaction conditions: 50.0 mg of catalyst; 1 mmol of benzyl alcohol $t = 2$ h and 15 mL of toluene as solvent; $T = 110$ °C. [b]Conversion (% based on benzyl alcohol. Conversion (%) based on substrate = [1 - ((concentration of substrate left after reaction) × (initial concentration of substrate))$^{-1}$] × 100. [c]Selectivity based on benzyl aldehyde no other products were detected. [d]TON − [(mol$_{substr}$)(mol$_{catalyst}$)$^{-1}$] where mol$_{substr}$ is the moles of benzyl alcohol converted. [e]Conversion in inert (N$_2$) atmosphere. [f]First recovery, mass of the catalyst recovered was 38 mg. [g]Second recovery, mass of the catalyst recovered was 20 mg. [h]Calculated conversion for fresh catalyst.

Publication list (including patents) acknowledging the DOE grant or contract

1. Qiu, G.; Dharmarathna, S.; Zhang, Y.; Opembe, N.; Huang, H.; Suib, S., Facile Microwave-Assisted Hydrothermal Synthesis of CuO Nanomaterials and Their Catalytic and Electrochemical Properties, *J. Phys. Chem. C*, **2012**, *116*, 468-477.

2. Chen, C.H.; Suib, S.L., Control of Catalytic Activity Via Porosity, Chemical Composition, And Morphology of Nanostructured Porous Manganese Oxide Materials, *J. Ch. Chem. Soc.*, 2012, *59*, 465-472.

3. Genuino, H.C.; Horvath, D.T.; King'ondu, C.K.; Hoag, G.E.; Collins, J.B.; Suib, S.L., Effects of visible and UV light on the characteristics and properties of crude oil-in-water emulsions, *Photochem. Photobiol. Sci.*, **2012**, *11*, 692-702.

4. Dharmarathna, S.; King'ondu, C.K.; Pedrick, W.; Pahalagedara, L.; Suib, S.L., Direct Sonochemical Synthesis of Manganese Octahedral Molecular Sieve (OMS-2) Nanomaterials Using Cosolvent Systems, Their Characterization, and Catalytic Applications, *Chem. Mat.*, **2012**, *24*, 705-712.

5. Njagi, E.C.; Genuino, H.C.; King'ondu, C.K.; Dharmarathna, S.; Suib, S.L., Catalytic Oxidation of Ethylene at Low Temperatures Using Porous Copper Manganese Oxides, *Appl. Catal. A*, **2012**, *421-422*, 154-160.

6. Opembe, N.N.; King'ondu, C.K.; Suib, S.L., Efficient Oxidation of 2,3,6-Trimethyl Phenol Non-Exchanged and H+ Exchanged Manganese Oxide Octahedral Molecular Sieves (K-OMS-2 and H–K-OMS-2) as Catalysts, *Catal. Lett.*, **2012**, *142*, 427-432.

7. Iyer, A.; Del-Pilar, J.; King'ondu, C.; Kissel, E.; Garces, H.; Huang, H.; El-Sawy, A.; Dutta, P.; Suib, S., Water Oxidation Catalysis using Amorphous Manganese Oxides, Octahedral Molecular Sieves (OMS-2) and Octahedral Layered (OL-1) Manganese Oxide Structures, *J. Phys. Chem. C*, 2012, *116*, 6474-6483.

8. Suib, S.L., Novel catalysts for oxidations, biomass conversion, and alternative fuels, *Preprints – American Chemical Society, Division of Petroleum Chemistry*, **2012**, *57*, 173-174.

9. Garces, H.F.; Espinal, A.E.; Suib, S.L., Tunable Shape Microwave Synthesis of Zinc Oxide Nanospheres and Their Desulfurization Performance Compared with Nanorods and Platelet-Like Morphologies for the Removal of Hydrogen Sulfide, *J. Phys. Chem. C*, **2012**, *116*, 8465-8474.

10. Espinal, L.; Wong-Ng, W.; Kaduk, J.A.; Allen, A.J.; Snyder, C.R.; Chiu, C.; Siderius, D.W.; Li, L., Cockayne, E., Espinal, A.E.; Suib, S.L., Time dependent CO_2 sorption hysteresis by octahedral molecular sieves with manganese oxide framework, *J. Am. Chem. Soc.*, **2012**, *134*, 7944-7951.

11. Genuino, H.; Dharmarathna, S.; Njagi, E.; Mei, M.; Suib, S., Gas-Phase Total Oxidation of Benzene, Toluene, Ethylbenzene, and Xylenes Using Shape-Selective Manganese Oxide and Copper Manganese Oxide Catalysts, *J. Phys. Chem. C*, **2012**, *116*, 12066-12078.

12. Genuino, H.; Hamal, D.; Fu, Y.J.; Suib, S., Synergetic Effects of Ultraviolet and Microwave Radiation for Enhanced Activity of TiO_2 Nanoparticles in Degrading Organic Dyes Using a Continuous-Flow Reactor, *J. Phys. Chem. C*, **2012**, *116*, 14040-14051.

13. Sharma, H.; Pahalagedara, L.; Joshi, A.; Suib, S.; Mhadeshwar, A., An Experimental Study of Carbon Black and Diesel Engine Soot Oxidation Kinetics using Thermogravimetric Analysis, *Energy Fuels*, 2012, in press.

14. Najafpour, M.M.; Sedigh, D.J.; King'ondu, C.K.; Suib, S.L., Nano-sized manganese oxide–bovine serum albumin as a promising and biomimetic catalyst for water oxidation, *RSC Adv.*, **2012**, 1-5.

15. Poyraz, A.S.; Biswas, S.; Genuino, H.C.; Dharmarathna, S.; Kuo, C.H.; Suib, S.L., Bimodification of Mesoporous Silicon Oxide by Coupled "In Situ Oxidation at the Interface and Ion Exchange" and its Catalytic Activity in the Gas-Phase Toluene Oxidation, *ChemCatChem*, **2012**, in press.

16. Hu, B.; Frueh, S.; Garces, H.F.; Zhang, L.; Aindow, M.; Brooks, C.; Kreidler, E.; Suib, S.L., Selective Hydrogenation of CO_2 and CO to Useful Light Olefins over Octahedral Molecular Sieve Manganese Oxide Supported Iron Catalysts, Appl. Catal. B, **2012**, 54-61.

17. Hu, B.; Suib, S.L., Synthesis of Useful Compounds from CO_2, in Green CO_2: Advances in CO_2 Utilization, G. Centi, S. Perathoner, Eds., John Wiley and Sons, Inc., NY, Chapter 3, 2013, in press.

18. Najafpour, M.M.; Leonard, K.C.; Fan, F.F.; Tabrizi, M.A.; Bard, A.J.; King'ondu, C.; Suib, S.L.; Haghighi, B.; Allakhverdiev, S.I.; Nano-size layered manganese-calcium oxide as an efficient and biomimetic catalyst for water oxidation under acidic conditions: comparable to platinum *Dalton Trans.*, **2013**, *42*, 5085-5091.

19. Genuino, H.; Meng, Y.; Horvath, D.T.; Kuo, C.H.; Seraji, M.S.; Morey, A.M.; ,Joesten, R.; Suib, S.L., Enhancement of Catalytic Activities of Octahedral Molecular Sieve Manganese Oxide for Total and Preferential CO Oxidation via Vanadium Ion Framework Substitution, *Chem Cat Chem*, **2013**, in press.

20. Hu, B.; Guild, C.; Suib, S.L., Thermal, Electrochemical, and Photochemical Conversion of CO_2 to Fuels and Value-added Products, *J. of CO_2 Util.*, **2013**, in press.