FINAL TECHNICAL REPORT

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Title: Templating Routes to Supported Oxide Catalysts by Design

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Performing Organization: Northwestern University, Evanston IL

Reporting Period: September 1, 2011 to August 31, 2015

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Abstract

The rational design and understanding of supported oxide catalysts requires at least three advancements, in order of increasing complexity: the ability to quantify the number and nature of active sites in a catalytic material, the ability to place external controls on the number and structure of these active sites, and the ability to assemble these active sites so as to carry out more complex functions in tandem. As part of an individual investigator research program that is integrated with the Northwestern University Institute for Catalysis in Energy Processes (ICEP) as of 2015, significant advances were achieved in these three areas. First, phosphonic acids were utilized in the quantitative assessment of the number of active and geometrically-available sites in MOx-SiO_2 catalysts, including nanocrystalline composites, co-condensed materials, and grafted structures, for M=Ti, Zr, Hf, Nb, and Ta. That work built off progress in understanding supported Fe, Cu, and Co oxide catalysts from chelating and/or multinuclear precursors to maximize surface reactivity. Secondly, significant progress was made in the new area of using thin oxide overcoats containing 'nanocavities' from organic templates as a method to control the dispersion and thermal stability of subsequently deposited metal nanoparticles or other catalytic domains. Similar methods were used to control surface reactivity in SiO_2-Al_2O_3 acid catalysts and to control reactant selectivity in Al_2O_3-TiO_2 photocatalysts. Finally, knowledge gained from the first two areas has been combined to synthesize a tandem catalyst for hydrotreating reactions and an orthogonal tandem catalyst system where two subsequent reactions in a reaction network are independently controlled by light and heat. Overall, work carried out under this project significantly advanced the knowledge of synthesis-structure-function relationships in supported oxide catalysts for energy applications.

Goals and DOE Interest. Techniques to design and synthesize supported oxide domains on the atomic scale remain a long-standing DOE grand challenge that will enable findings from structural and functional studies to be translated into new catalyst designs in a rational manner. Critically, improved understanding and control of individual sites promises to lead to the assembly of individual sites into more complex structures by design, enabling tandem reactions and multifunctional catalysts with greatly improved process efficiencies and selectivity.

Specifically sought here was an understanding of the requirements for synthesizing and stabilizing isolated metal cations and small supported oxide clusters, methods for evaluating these nanoscale domains, and methods for incorporating them into larger functional assemblies. These larger assemblies included controlling small metal nanoparticle domains within oxide structures, controlling the reactivity at the interface of two oxides, such as in SiO_2-Al_2O_3 materials or doped, supported oxides, or combining two distinct modes of reaction in tandem systems.

Area 1. Refining Synthesis-Structure-Function Relationships and Quantifying Active Site Densities. Starting in 2011, this research developed the use of bulky, strongly-chelating, and net anionic $[\text{M-EDTA}]^{n-}$ complexes as a route to control dispersion primarily in FeOx-SiO_2 and FeOx-CeO_2 materials, as well as for M = Cu, Co, and others. This type of precursor (the EDTA ligand) is readily available and inexpensive, and has been used previously with the goal of synthesizing relatively large domains of FeOx for applications in Fischer Tropsch catalysis and related reactions. Here, it was found that on SiO_2, the resulting materials were highly active for oxidations with H_2O_2. The bulky, strongly-chelating, and net anionic Fe-EDTA complexes enforced unusually high levels of dispersion for FeOx-SiO_2 catalysts, as judged by XPS, XANES, DRUV-vis, and TPR, particularly when alkali countercations were used in catalyst precursors (e.g. NaFeEDTA). [1] The latter precursor gave verifiably 'single-site' oxide catalysts (**Figure 1**) and using it as a starting point, a full map was developed for the reactivity of particular FeOx surface structures.[2] It was shown that alkane oxidation rates (with H_2O_2) increased with increasingly basic alkali countercations, and that the alkali was required to be in stoichiometric equivalence with Fe. Rates were shown to be independent of structure for isolated cations and very small clusters, but the latter were relatively uncommon (<10%) for typical catalyst preparations.

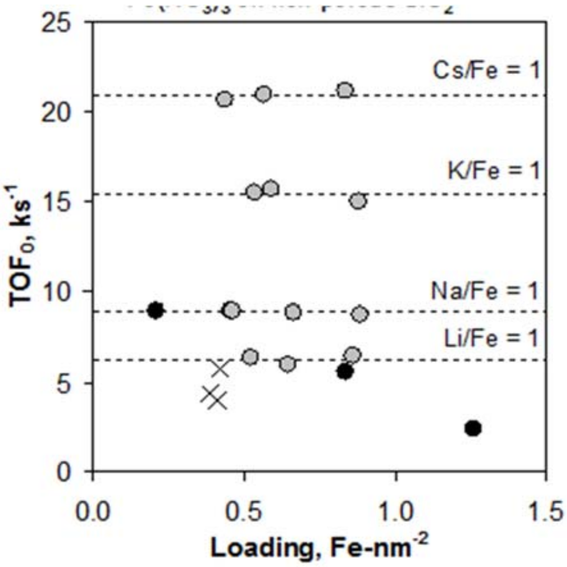


Figure 1. Alkali-dependent, single-site behavior (grey circles) in alkane oxidation over FeOx-SiO_2 using a Fe-EDTA precursor and a non-porous spherical silica support. X indicates a conventional precursor, and dark circles show the impact of pore collapse during catalyst pretreatments when using mesostructured catalysts.

On CeO_2, the EDTA precursor led to ~50% more redox-active sites than for more traditional precursors, due to the formation of sites consistent with very small clusters of FeOx. This improved activity in, for example, the reduction of NO with H_2 or CO, [3-5] a project that was carried out under other support following the initial development of this precursor described above. That work was also the basis for a patent application [6] and is being extended to selective hydrogenation reactions under other support.

This project also addressed the significant issue in supported oxide catalysts of quantifying catalytic rates per accessible surface atom. Dispersion (e.g. active sites per total metal) is not as readily measured as for supported metal catalysts, especially for light oxides, because typical chemisorption probes like CO or H_2 are ineffective, direct imaging is extremely challenging, EXAFS are difficult to fit to simple models of cluster size, and many materials of interest are not crystalline. We developed a phenylphosphonic acid (PPA) titration and applied it to a range of supported and mixed oxide materials synthesized by a number of different types of grafting and sol-gel. Using this method, two main findings were shown. First, using an aggressive addition of PPA, all geometrically-accessible TiOx sites could be titrated in a mixed oxide. (**Figure 2**) For most grafting techniques below monolayer coverage, nearly all sites were accessible, even though their structure may vary significantly by DRUV-vis or other spectroscopic techniques.[7] It was then shown that photocatalytic oxidations using these grafted materials were primarily determined by the number of solvent-accessible sites, rather than any other specific properties resulting from differences in surface coverage or grafting strategy – i.e. it was structure insensitive when light of sufficient intensity and energy was used. This titration for geometrically-accessible sites allowed the development of a new synthesis-structure-function map that included fine gradations between, for example, polymeric TiOx, 2D anatase-like surfaces, and nanocrystalline anatase, which had not been previously proposed.

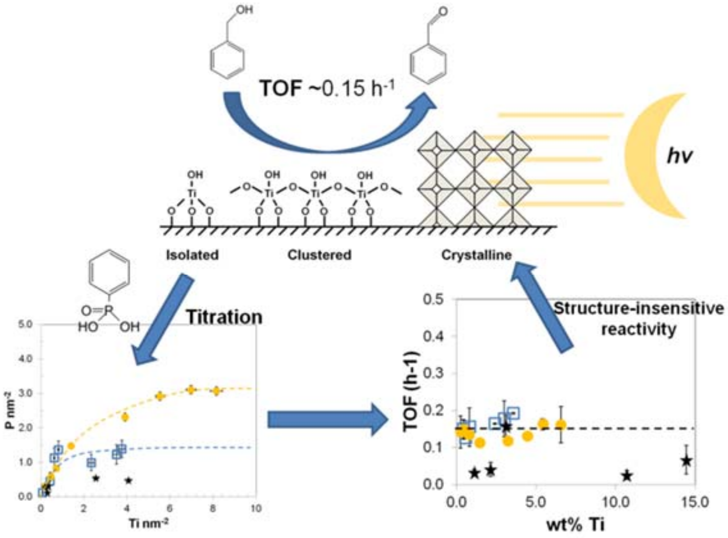


Figure 2. Benzyl alcohol oxidation, driven by UV illumination, was studied over TiO_2-SiO_2 materials synthesized by different methods and at different surface densities to give a range of 'isolated', polymeric sheets, and crystalline domains, then were titrated with phenylphosphonic acid. Grafting titanium ethoxide (circles) eventually led to near full coverage of the surface with crystalline anatase domains, wherase a titanocene precursor (squares) never crystallized, but also left a significant fraction of Ti unable to be titrated. Regardless of Ti electronic structure, normalizing rates of the supported species by titrate-able sites gave a single TOF.

Secondly, an *in situ* phosphonic acid titration method was used to assess the number of sites active in a liquid phase oxidation by MOx-SiO_2 catalysts. [8, 9] Phenylphosphonic acid added to the reaction mixture monotonically decreased the rate of cyclooctene epoxidation with H_2O_2 in acetonitrile over all TiOx-SiO_2, ZrOx-SiO_2, and HfOx-SiO_2 materials tested. NbOx-SiO_2 and TaOx-SiO_2 epoxidation rates appeared to have a second-order dependence on titrant, which is consistent with the kinetic relevance of a dihydroxy site in these materials.[9] From such plots, the intercept (or the value required to eliminate 95% of the activity) was set as the number of catalytically relevant sites; no assumptions or further characterization of the material were needed and thus this technique can be applied to 'unknown' samples. An extensive data set was developed for TiOx-SiO_2 and NbOx-SiO_2 with three significant findings: 1) some synthesis methods, such as the metallocalixarene route pioneered by the PI while still a PhD student, were quantitatively proven as the most disperse oxides, 2) mixed oxides that showed evidence of aggregation into crystallites were not necessarily poor catalysts, due to the simultaneous presence of highly dispersed active sites not counted by most bulk characterization techniques, and 3) using the *in situ* titration data, epoxidation rates were normalized over <u>*dozens*</u> of different supported oxide catalysts, showing that it was the number, not the intrinsic activity, that differed amongst the various materials. (**Figure 3**) This method is now being applied to many other classes of catalyst including crystalline materials (e.g. zeolites), to identify the very small numbers of undercoordinated active sites at interfaces of nanocrystalline materials, and to use different phosphonic acids as a potential method to probe sites with different geometrical restrictions. A review of this method is being prepared, which will hopefully see it adopted for other purposes.

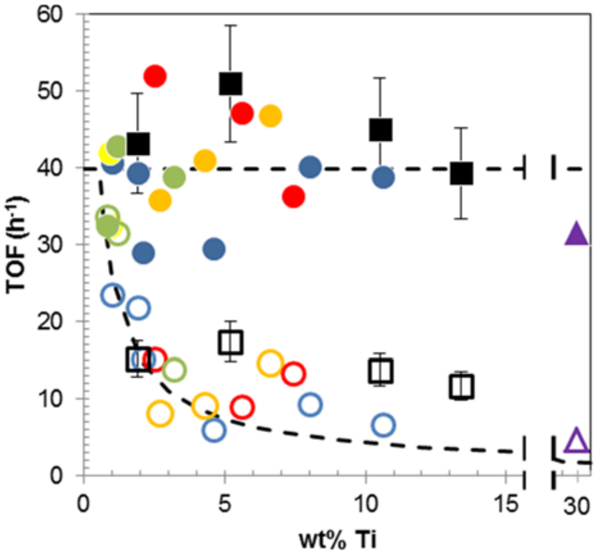
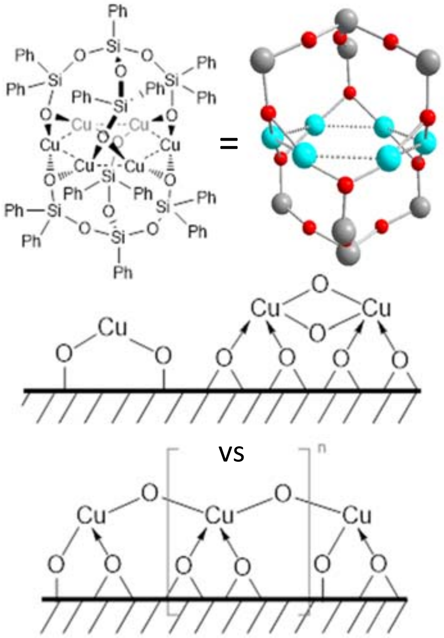
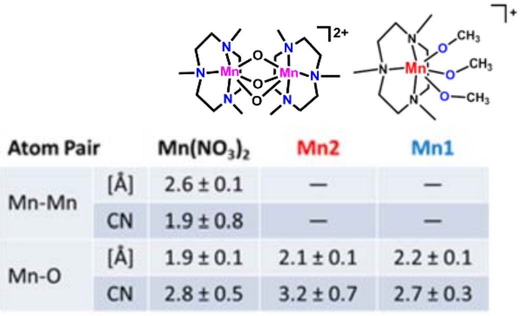


Figure 3. Cyclooctene epoxidation rates of 22 TiOx-SiO_2 catalysts were normalized by phenylphosphonic acid titration (filled) in ways not captured by typical correlations against total Ti content. (open)

***Area 2. Templating via Well-Defined Oxide Precursors*.** Here, this project sought to control supported oxide catalyst structure via precursor design. We originally investigated the use of supported Mn(IV) triazacyclononane (TACN) complexes of different nuclearity (mononuclear **Mn1**, dinuclear **Mn2**, and tetranuclear **Mn4**, Mn(IV) oxide complexes) as alkane oxidation catalysts. Immobilized onto carboxylate-functionalized surfaces, these are catalysts for room-temperature alkane oxidation and alkene epoxidation from the formation of carboxylate bridged structures of reduced oxidation state, as determined by EXAFS and XANES. [e.g. 10] When grafted to silica and calcined, precursors **Mn1**, **Mn2**, and **Mn4** led to unique structures of supported MnOx. After the complexes were deposited intact on SiO_2, all catalysts autoreduced to Mn(III) oxides at 250°C or above, when the ligand decomposed. After this mild calcination temperature, 1st shell Mn-O fits increased monotonically from the **Mn1**, **Mn2**, and **Mn4** precursors. (**Figure 4**) While unambiguous fits of such complex oxide structures were challenging, these results were consistent with higher nuclearity clusters from increasing nuclearity of the deposited precursor. With more aggressive calcination, **Mn1**, **Mn2**, and **Mn4** precursors had similar coordination environments, and had no strong evidence of Mn-Mn interactions, unlike for a typical $Mn(NO_3)_2$ precursor, which began to form small microcrystalline domains even at 0.5 wt% loading. While this work has not yet led to publication due to the generally poor low-temperature alkane oxidation reactivity of these materials, they remain a useful material in the PI's stable of catalysts, and the approach is expected to find utilization as we move to reactions such as oxidative coupling of methane, where manganese oxide dispersion on silica is expected to be critical.

Finally, a collaboration was initiated with the Humboldt University of Berlin wherein a hexameric Cu(I) complex was deposited on SiO_2 through wet impregnation from dry THF. This and related complexes have relatively short Cu-Cu distances (0.27 nm) and highly multidentate silanol ligands. These complexes are unstable in solution and oxidize irreversibly, but we collected evidence that they remained as stable Cu(I) complexes in the solid state to ~450°C, much like Cu-exchanged zeolites. After calcination, we demonstrated that these materials were active catalysts for cyclohexane oxidative dehydrogenation. [11] (**Figure 4**) We believe this to be the first report of ODH by supported copper oxides, and we also showed the importance of very small CuOx clusters that were produced in the highest amount from this multinuclear precursor, as compared to more conventional Cu sources.





Atom Pair		Mn(NO$_3$)$_2$	Mn2	Mn1
Mn-Mn	[Å]	2.6 ± 0.1	—	—
	CN	1.9 ± 0.8	—	—
Mn-O	[Å]	1.9 ± 0.1	2.1 ± 0.1	2.2 ± 0.1
	CN	2.8 ± 0.5	3.2 ± 0.7	2.7 ± 0.3

Figure 4. Well-defined supported metal oxides were derived from precursor complexes protected by bulky ligands. For example, monomeric and dimeric, cationic Mn trimethyltriazacyclononane complexes gave isolated Mn(III) structures, by EXAFS fitting, after 550°C calcination, wherase $Mn(NO_3)_2$ gave small Mn_2O_3 clusters at equal, low loadings. Similarily, hexameric Cu(I) clusters led to better reducability, smaller clusters sizes by DRUV-vis, and better reactivity in cyclohexane ODH than the same loadings from conventional precursors.

Area 3. Templating via Support Design. As part of this research grant, we developed carrier (oxide) particles partially overcoated with <2nm of a second oxide by repetitive growth methods such as ALD or limiting alkoxide addition in solution for use as catalysts or catalyst supports. Molecular templates were used to generate nanocavities (nc) ~2 nm in diameter whose walls and floor were different oxide compositions. This synthesis strategy and its subsequent uses are illustrated in **Figure 5.** We first showed that Al_2O_3-nc-TiO_2 imparted reactant selectivity to oxidations and reductions catalyzed by the underlying TiO_2.[12] For example, in the oxidation of equimolar benzyl alcohol and more bulky alcohols to their respective aldehydes, relative rates increased from ~1.5:1 for TiO_2 to nearly 10:1 for the overcoated materials. Such selectivity had not, to our knowledge, been previously demonstrated in a formally non-porous oxide catalyst. We are developing a library of supports, templates, and oxide deposition techniques to expand this approach.

Secondly, we showed that SiO_2-nc-TiO_2 allowed for the selective photodeposition of Ag nanoparticles onto small domains of exposed TiO_2, decreasing the average Ag particle size and polydispersity, as well as improving its thermal stability.[13] We also recently showed a similar improvement for Pt deposited by traditional incipient wetness impregnation,[14] implying that the Pt nanoparticles migrate to SiO_2-TiO_2 interfaces where they are stabilized. As extensions for the successor program, we are also applying these supports to the selective metal deposition methods such as strong electrostatic adsorption to further control metal nanoparticle size and stability. These methods for improving supported metal nanoparticle dispersion and stability are applicable to many reactions and are being applied in the successor program and in other areas.

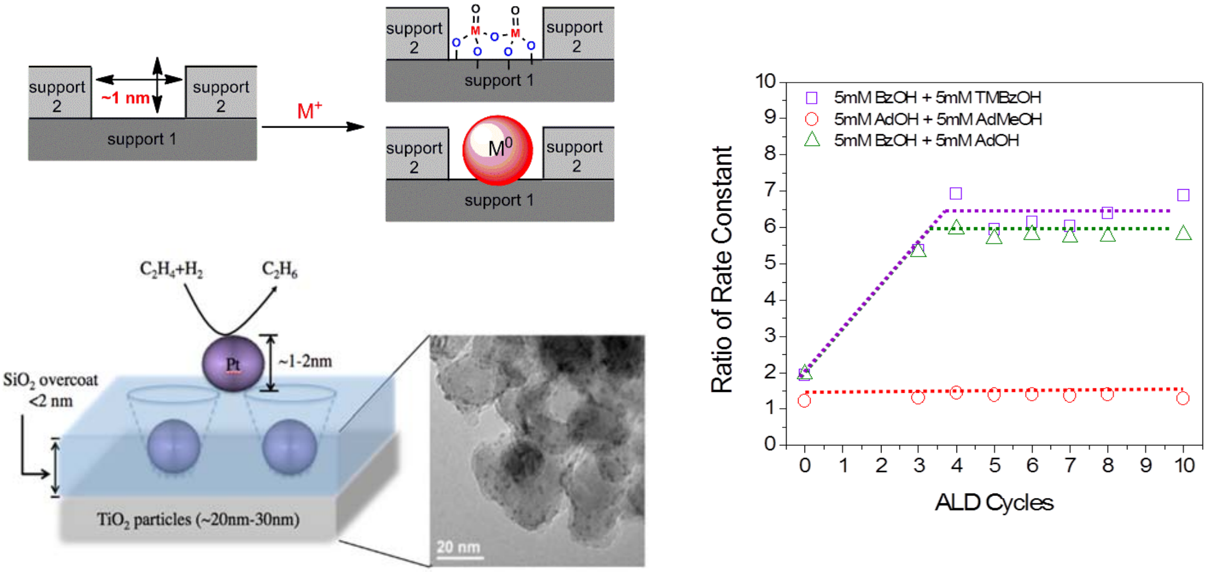


Figure 5. Cartoon illustrating the use of 'nanocavity' oxides to template formation of supported oxide or metal domains exploiting strong electrostatic adsorption or stronger metal-support interactions. For example, with support 1 = TiO_2, and 2 = SiO_2, the SiO_2 regions are expected to be more negatively charged than the TiO_2, giving preferential deposition of anionic precursors (ie chloroplatinate or permanganate) at the nanocavities, while also stabilizing the formed metal nanoparticles, as shown to be successful for <2 nm Pt nanoparticles. Alternately, the nanostructured support itself can be used as a selective catalyst, as was shown for competitive alcohol oxidation, where relative rates stabilized out at ~6:1 favoring the less hindered alcohol over a calcined Al_2O_3-nc-TiO_2.

An open goal being addressed in successor programs is to use the nanocavity space to template the growth of oxide catalyst domains, particularly of redox-active clusters, the importance of which has been demonstrated in other areas supported by this project. In addition, detailed investigations are being carried out on the catalytic consequences of template surface density and template size used during syntheses of oxide overcoats of different thicknesses. In parallel, the successor program is also beginning an examination of the Lewis- and Brønsted-acidic SiO_2-Al_2O_3 interface developed from the templated oxide deposition. In this work, we have shown that strong acidity develops at appropriate thicknesses of the SiO_2 overcoat, and this acidity can be enhanced by particular catalyst pretreatments.[15] These catalysts are active in alkane cracking, and may lead to a new class of highly tunable acid catalysts with negligible intrapore diffusion limitations.

Area 4. Tandem Catalysis

Parallel work partially supported by this program has focused on developing and understanding routes to combine multiple functionalities in oxide catalysis. In one area, we demonstrated that Al_2O_3-supported TaOx and other oxides assists in the Pd-catalyzed hydrodenitrogenation of quinoline and anilines.[16] These reactions are critical for processing of certain crudes. The added Lewis sites were shown in separate experiments to be capable of direct C-N bond hydrogenolysis on their own, but this reaction was stoichiometric. However, they also catalytically turnover for deamination reactions,[17] consistent with the hypotheses that the Lewis sites selectively deaminated partially hydrogenated intermediates coming from the Pd nanoparticles during quinoline hydrodenitrogenation. Regardless of mechanism, the net effect was to decrease the H_2 required for a given level of N removal by encouraging deamination and the production of aromatic products (e.g. propylbenzene), rather than hydrogenolysis that produces fully saturated products. A review was also published in this area.[18]

Finally, work in area 1 allowed particular types of oxide sites (e.g. isolated sites vs. extended oxide surfaces) to be synthesized deliberately and with known numbers. Work in area 3 allowed different sites to be isolated spatially from one another on the nm-length scale. With these two tools in hand, orthogonal tandem catalysts were synthesized, wherein two separate surfaces independently operated on different reactants in a reaction network occurring in a reaction vessel. As a proof of concept, we overcoated TiO_2 nanoparticles with SiO_2, as in area 3. This still allowed the photocatalytic oxidation of isopropanol with O_2 to produce acetone and H_2O_2 selectively. Isolated Ti-SiO_2 sites were then grafted to the external surface, and these sites scavenged the produced H_2O_2, allowing the selective oxidation of alkenes to epoxides to proceed. (**Figure 6**) Each of the two oxidation reactions were independently controllable, even though they occured simultaneously in the same pot and same particle. This has led to an invention disclosure and patent application, and will be followed up shortly with a manuscript submission. We believe this to be the first demonstration of a selective, orthogonal tandem reaction combining photocatalysis and traditional thermocatalysis. [19] Many other selective oxidations are envisioned using this catalyst platform, which we hope to investigate with future support. In addition to the specific application described here, these types of materials are a route to combine isolated Lewis acid sites and reducible supports, which cannot otherwise be done.

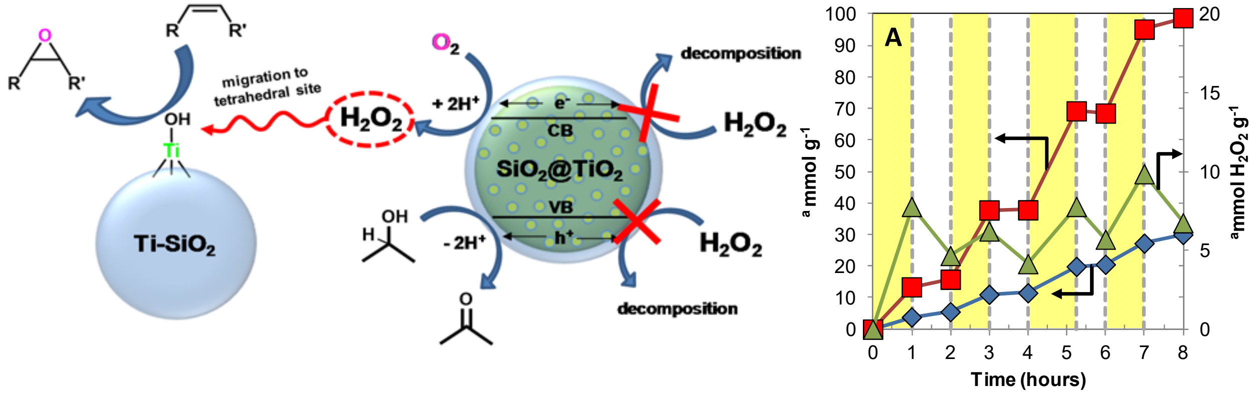


Figure 6. Ti-SiO_2-TiO_2 materials were demonstrated as tandem photo-thermal catalysts for the synthesis of H_2O_2 over illuminated TiO_2 and its use for epoxidation over Ti-SiO_2 sites on the same or different particles. □, mmol/g acetone from photocatalytic oxidation; ◊, mmol/g epoxide from full tandem reaction; Δ, mmol/g H_2O_2 produced from photocatalytic oxidation and consumed by the thermocatalyst. Illumination only during yellow bars.

PUBLICATIONS and PATENT APPLICATIONS RESULTING FROM DE-SC0006718 (numbers link to text)

[1] D. Prieto-Centurion, J. M. Notestein*, "Surface speciation and alkane oxidation with isolated Fe sites on silica," J. Catal., 2011, 279, 103-110.

[2] D. Prieto-Centurion, A. M. Boston, J. M. Notestein*, "Structural and electronic promotion with alkali cations of silica-supported Fe(III) sites for alkane oxidation," J. Catal., 2012, 296, 77-85.

[3] D. Prieto-Centurion, T. R. Eaton, C. A. Roberts, P. T. Fanson, J. M. Notestein, J. M.*, "Catalytic reduction of NO with H2 over redox-cycling Fe on CeO2," Appl. Catal. B, 2015, 168, 68-76.

[7] T. R. Eaton, M. P. Campos, K. A. Gray, J. M. Notestein,* "Quantifying accessible sites and reactivity on titania-silica (photo)catalysis: Refining TOF calculations," J. Catal. 2014, 309, 156-165.

[8] T. R. Eaton, A. M. Boston, A. B. Thompson, K. A. Gray, J. M. Notestein*, "Counting Active Sites on Titanium Oxide–Silica Catalysts for Hydrogen Peroxide Activation through In Situ Poisoning with Phenylphosphonic Acid," ChemCatChem 2014, 6, 3215-3222.

[12] C. P. Canlas, J. Lu, N. A. Ray, N. A. Grosso-Giordano, J. W. Elam, S. Lee, R. E. Winans, P. C. Stair, R. P. Van Duyne, and J. M. Notestein*, "Shape-Selective Sieving Layers on an Oxide Catalyst Surface," Nature Chem., 2012, 4, 1030-1036.

[13] Z. Bo, T. R. Eaton, J. R. Gallagher, C. P. Canlas, J. T. Miller, J. M. Notestein*, "Size-selective synthesis and stabilization of small Ag nanoparticles on TiO2 partially masked by SiO2," Chem. Mater. 2015, 27, 1269-1277.

[16] M. Bachrach, N. Morlanes, C. P. Canlas, J. T. Miller, T. J. Marks, J. M. Notestein*, "Increasing the Aromatic Selectivity of Quinoline Hydrogenolysis Using Pd/MOx–Al2O3," Catal. Lett. 2014, 144, 1832-1838.

[17] M. Bachrach, T. Marks*, J. M. Notestein*, "C-N bond hydrogenolysis of aniline and cyclohexylamine over TaOx-Al2O3," New J. Chem., 2016, 7, 6001-6004.

[18] Bachrach, M.; Marks, T.*; Notestein, J. M.*, "Understanding the Hydrodenitrogenation of Heteroaromatics on a Molecular Level," ACS Catal., 2016, 6, 1455-1476.

[19] "Catalysts and Related Methods for Photocatalytic Production of H2O2 and Thermocatalytic Reactant Oxidation," K. A. Gray, J. M. Notestein, T. R. Eaton, Application US2016023044, 2016.

PUBLICATIONS ACKNOWLEDGING SUCCESSOR PROGRAM, DE-FG02-03-ER154757 (numbers link to text)

[11] S. L. Nauert, F. Schax, C. Limberg, J. M. Notestein*, "Cyclohexane oxidative dehydrogenation over copper oxide catalysts," J. Catal., 2016, 341, 180-190.

[14] Z. Bo, S. Ahn, M. A. Ardagh, N. M. Schweitzer, C. P. Canlas, O. K. Farha, J. M. Notestein*, "Synthesis and Stabilization of Small Pt Nanoparticles on TiO2 Partially Masked by SiO2," submitted, under revision, 2016

[15] M. A. Ardagh, Z. Bo, S. L. Nauert, J. M. Notestein*, "Depositing SiO2 on Al2O3: a route to tunable Bronsted acid catalysts," ACS Catal., 2016, 6, 6156-6164.

ALL REFERENCES CITED

[1] D. Prieto-Centurion, J. M. Notestein*, "Surface speciation and alkane oxidation with isolated Fe sites on silica," J. Catal., 2011, 279, 103-110.

[2] D. Prieto-Centurion, A. M. Boston, J. M. Notestein*, "Structural and electronic promotion with alkali cations of silica-supported Fe(III) sites for alkane oxidation," J. Catal., 2012, 296, 77-85.

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[4] Roberts, C. A.*; Prieto-Centurion, D.; Nagai, Y.; Nishimura, Y. F.; Desautels, R.; van Lierop, J.; Fanson, P. T.; Notestein, J. M.*, In Situ Characterization of highly dispersed, ceria-supported Fe sites for NO reduction by CO. J. Phys. Chem. C 2015, 119, 4334-4234.

[5] C. A. Roberts*, L. Savereide, D. J. Childers, T. C. Peck, J. M. Notestein, "In situ FTIR spectroscopy of highly dispersed FeOx catalysts for NO reduction: Role of Na promoter," Catal. Today, 2016, 267, 56-64.

[6] "Fabrication of catalyst used in catalytic converter of automotive vehicle, involves contacting substrate containing with transition/post transition metal, and contacting substrate with alkali/alkaline earth metal cations", J. M. Notestein, D. Prieto-Centurion, P. T. Fanson, C. A. Roberts, Applications WO2015077268, US20150139883, 2015.

[7] T. R. Eaton, M. P. Campos, K. A. Gray, J. M. Notestein,* "Quantifying accessible sites and reactivity on titania-silica (photo)catalysis: Refining TOF calculations," J. Catal. 2014, 309, 156-165.

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[9] N. E. Thornburg, S. L. Nauert, A. B. Thompson, J. M. Notestein, "Synthesis-structure-function relationships of silica-supported niobium(V) catalysts for alkene epoxidation with H2O2," ACS Catal., 2016, 6, 6124-6134.

[10] P. A. Ignacio de Leon, C. A. Contreras, N. E. Thornburg, A. B. Thompson, J. M. Notestein*, "Catalyst structure and substituent effects on epoxidation of styrenics with immobilized Mn(tmtacn) complexes," Appl. Catal. A., 2016, 511, 78-86

[11] S. L. Nauert, F. Schax, C. Limberg, J. M. Notestein*, "Cyclohexane oxidative dehydrogenation over copper oxide catalysts," J. Catal., 2016, 341, 180-190.

[12] C. P. Canlas, J. Lu, N. A. Ray, N. A. Grosso-Giordano, J. W. Elam, S. Lee, R. E. Winans, P. C. Stair, R. P. Van Duyne, and J. M. Notestein*, "Shape-Selective Sieving Layers on an Oxide Catalyst Surface," Nature Chem., 2012, 4, 1030-1036.

[13] Z. Bo, T. R. Eaton, J. R. Gallagher, C. P. Canlas, J. T. Miller, J. M. Notestein*, "Size-selective synthesis and stabilization of small Ag nanoparticles on TiO2 partially masked by SiO2," Chem. Mater. 2015, 27, 1269-1277.

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[15] M. A. Ardagh, Z. Bo, S. L. Nauert, J. M. Notestein*, "Depositing SiO2 on Al2O3: a route to tunable Bronsted acid catalysts," ACS Catal., 2016, 6, 6156-6164.

[16] M. Bachrach, N. Morlanes, C. P. Canlas, J. T. Miller, T. J. Marks, J. M. Notestein*, "Increasing the Aromatic Selectivity of Quinoline Hydrogenolysis Using Pd/MOx–Al2O3," Catal. Lett. 2014, 144, 1832-1838.

[17] M. Bachrach, T. Marks*, J. M. Notestein*, "C-N bond hydrogenolysis of aniline and cyclohexylamine over TaOx-Al2O3," New J. Chem., 2016, 7, 6001-6004.

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[19] "Catalysts and Related Methods for Photocatalytic Production of H2O2 and Thermocatalytic Reactant Oxidation," K. A. Gray, J. M. Notestein, T. R. Eaton, Application US2016023044, 2016.