THE SCOTT GROUP

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Overview

The Scott group conducts both fundamental and applied research in surface chemistry and catalysis. We aim to understand the interactions and transformations of molecules in solution and at gas-solid interfaces by creating highly uniform, grafted active sites. We apply techniques from organometallic and coordination chemistry, surface science, spectroscopy, kinetics, mechanistic analysis and modeling to investigate, design and re-engineer heterogeneous catalysts. The group is comprised of researchers in chemistry and chemical engineering working together to solve problems at the interface of chemistry and reaction engineering.

Redox Reactions Catalyzed by PGM-Substituted Complex Oxides



DFT model for Pd-substituted BaCeO₃. Pd (blue) is substituted on a Ce (yellow) site, and is accompanied by an O (orange) vacancy. Ba cations are shown in grey.



The incorporation of Pt-group metals (PGMs) into *crystalline* complex oxide hosts (e.g., the perovskite, in the example on the left) facilitates structural characterization and the direct comparison of experiment with theory. With these materials, we aim to tailor highly active and robust catalysts for the oxidation of CO and the reduction of NO_x emissions in automotive exhaust streams.

The low surface areas of perovskites do not preclude high catalytic activity, and their high thermodynamic stability may be a significant benefit. Both BaO and CeO₂ are stabilized against deactivation when combined as BaCeO₃. Perovskite lattice (surface + bulk) oxygen promotes oxidation reactions at surface Pd sites. High lattice mobility is due to increased vacancy concentration associated with the presence of Pd(II) in the bulk.

CO-lean conditions	Langmuir-Hinshelwood mechanism (LH)	$rate(LH) = \frac{2k_2P(O_2)}{1 + K_1P(CO)} \approx \frac{2k_2P(O_2)}{K_1P(CO)}$
CO-rich conditions	BaCeO ₃ -mediated mechanism (BC)	$rate(BC) = 2k_{4'}\theta(CO)\theta(O_L) \approx 2k_{4'}$
Near-stoichiometric conditions $(1 \le P(CO))/P(O_2) \le 10)$	Langmuir-Hinshelwood and BaCeO ₃ -mediated mechanisms	rate = rate(LH) + rate(BC)

P(CO), the reaction is strongly CO-inhibited. When high P(CO) causes nearly all the

New Catalysts for Converting Biomass to Fuels and Chemicals

This project targets the development of solid catalysts for the efficient conversion of non-food biomass feedstocks (lignocellulose and soluble carbohydrates) to fuels and platform chemicals. One such reaction is the dehydration of sugars to 5-hydroxymethylfurfural (HMF), for which we designed an ordered mesoporous acid catalyst. The tandem hydrogenation or oxidation of HMF using a second, supported catalyst is underway.



Improving the hydrothermal stability of mesoporous organosilica catalysts The reaction conditions (130°C in water) cause loss of activity due to cleavage of the functional groups. Incorporating ethylene groups into the framework makes the catalyst more hydrophobic and increases its lifetime.



When Si(OEt)₄ (TEOS) is cocondensed with an organosilane RSi(OMe)₃ (TESAS, containing both thioether and sulfonic acid functional groups) in the presence of a block copolymer surfactant (Pluronic 123) and NaCl, it forms hexagonallyordered micelles.



After extraction of the surfactant, the remaining amorphous silica has the hexagonally mesoporous SBA-15 structure and contains the TESAS organic groups in the pores. The thioether can be oxidized by H_2O_2 during synthesis to the sulfoxide or the sulfone, which may be reaction promoters because they favor the tautomerization of fructose to the desired furanose form. However, they also make the pores more hydrophilic, and the thioether form of the catalyst was actually found to be the most selective.

A vanadium catalyst based on hydroxyguinoline-modified silica Chemical catalytic conversion of lignocellulose to value-added feedstocks would represent a major breakthrough towards production of bio-derived energy. A heterogeneous vanadium catalyst for oxidative C-C cleavage is designed to be a robust and reusable means to execute this transformation





Pd K-edge EXAFS of Pd-substituted BaCeO₃, showing curvefit to the DFT model. This confirms square-planar coordination of Pd with an accompanying O vacancy.

accessible Pd sites to be poisoned, a new mechanism involving lattice oxygen becomes available. This catalyst shows much higher activity than conventional catalysts such as Pd/Al₂O₃ under both types of reaction conditions.

See J. Catal. 2010, 273, 83; Inorg. Chem., 2010, 49, 4670; Chem. Mater. 2008; 20, 6567; J. Catal., 2007, 249, 349; Chem. Mater. 2007, 19, 1418.

Controlled, Autocatalytic Synthesis of Metal Nanoparticles

Metal nanoparticles dispersed on oxide supports show high activity and selectivity in oxidation, including low-temperature CO oxidation. We are exploring the scaleable synthesis of uniform, supported metal nanoparticles using molecular precursors. $(CH_3)_2Au(acac)$ (acac = acetylacetonate) can be dispersed on oxides by chemical vapor deposition. With mild heating it is transformed to gold nanoparticles. The process can be monitored in situ by IR. Autocatalysis is clearly evident in the kinetics, providing fundamental information about the rates of particle nucleation and growth. By varying the support and the reaction conditions, we can establish the requirements for particle size selection.





150

Time (min)

200

🔺 1603 cm

250

Curvefitting of timeresolved IR spectra can be used to extract rate constants $1566~\mathrm{cm}^$ for the biphasic, autocatalytic 1692 cm⁻ transformation of $(CH_3)_2Au(acac)$ to AuNPs on silica

DFT models for the organogold precursor and the hydroxylterminated silica surface predict adsorption via H-bonding

See J. Phys. Chem. C 2009, 113, 8794; J. Chem. Crystallogr. 2009, 39, 173; Spectrochim. Acta 2008, 71, 969.

Alkene and Alkane Metathesis

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We aim to understand the activation and deactivation of supported olefin metathesis catalysts such as perrhenate (ReO_{4}) on alumina and methyltrioxorhenium (MTO) on silica-alumina, in order to develop rational ways to increase their productivity and extend the range of viable substrates to biomass-derived olefins such as unsaturated seed oils. Important questions include how the first metal-carbene active sites are formed, and how they interact with Lewis bases and polar molecules.



Green: SiO₂-PrSO₃H; Blue: SBA-15-PrSOH₃H Red: SBA-15-45%Et-PrSOH₃H; Black: SBA-15-90%Et-PrSOH₃H See Topics Catal. 2010, 53, 1185; Green Chem. 2010, 12, 1640.

Supported Olefin Polymerization Catalysts

We investigate the relationships between active site structures and polymerization activity for heterogeneous Phillips' (Cr) and Ziegler-Natta (Ti, V) catalysts, as well as supported single-site catalysts. Frequently, the catalystsupport interaction is crucial to the appearance of activity. Grafting of $B(C_6F_5)_3$ onto silica to create a robustlyanchored co-catalyst for single-site olefin polymerization has been achieved for the first time in our lab. The reaction is catalyzed by trace water, which can be generated *in situ* by borane-induced dehydroxylation of surface silanols, or added intentionally. The grafted borane is a well-defined, supported Lewis acid that activates molecular complexes of Cr and Ni for olefin polymerization.





and (b) after modification with excess $B(C_6F_5)_3$, in the presence of 0.1 equiv. H_2O as catalyst.

See J. Catal. 2009, 262, 44; J. Phys. Chem. C 2008, 112, 6439; Chem. Commun. 2008, 4186; Inorg. Chim. Acta 2008, 361, 3315.

Spatial Distribution of Grafting Sites on Silica

Amorphous silica is an important support for many heterogeneous catalysts. It also has one of the simplest oxide surfaces, possessing only weakly Brønsted acidic hydroxyl groups, siloxane bonds and no Lewis acid sites. The hydroxyl groups represent the principal grafting sites for molecular catalysts. It is widely assumed that they become isolated during thermal pretreatment of the silica. We probed the distribution between the hydroxyls by studying their interaction with $Ga(CH_3)_3$.



(a) The Ga K-edge EXAFS (FT magnitude: red; imaginary: black) for a Ga(CH₃)₃-modified silica (A380-800), showing the curve-fit (blue) to model **3** (blue), with fixed N = 1 for the Ga-Ga path; and (b) analysis of optimum N for the Ga-Ga path, via the correlation-break method.

A computational (DFT) model shows a strong energetic preference for dimer formation from vicinal silanols reacting with Ga(CH₃)₃:



Even after heating silica at 800 °C, the EXAFS shows that only disilanolate-bridged digallium sites are formed, implying that the hydroxyl groups are paired (and probably vicinal). This unexpected finding opens the door to the design of cooperative catalysts with localized order in dissimilar sites.

See J. Am. Chem. Soc., 2011 (in press) and Organometallics 2006, 25, 1891.

New Spectroscopic and Kinetic Methods for Catalysis

Wavelet Transform EXAFS (2D EXAFS analysis) 2D WT-EXAFS can help identify scattering paths that overlap in the 1D FT-EXAFS. This new approach shows that dimolybdate sites are present in Mo/HZSM-5.

Operando FTIR Spectroscopy

	0.20
A CO-lean mixture of CO/	250
O ₂ flowing over a Pd/Al ₂ O ₂	200

140

130

120

100

1875

110 റ



Microkinetic model for the self-metathesis of propylene. Re and Re* denote unactivated and activated sites, respectively. The activated sites comprise both Re=CH₂ and Re=CHCH₃.

$$Re^{-} + \frac{k_{1}}{k_{.1}} Re^{-} + \frac{k_{2}}{k_{.2}} Re^{-} + \frac{k_{2}}{k_{.2}}$$

80 40 Partial 05 Products 20 10 20 30 40 50 60 70 80 Time (min)

The curvefits (lines) are shown for the microkinetic model with (red) and without (blue) the activation step. When measured as a function of temperature, the activation rate constant k_{act} shows the expected Arrhenius behavior, but the apparent propagation rate constants increase as the temperature decreases. This apparent negative activation energy suggests that the steady-state number of active sites decreases with increasing temperature, i.e., deactivation is faster than reactivation.

An important application for this work is alkane metathesis, in which alkane dehydrogenation and olefin metathesis are coupled using a tandem catalyst system. It results in homologation of short-chain hydrocarbons so that they can be used as fuels (diesel-range). The lifetime of the olefin metathesis catalyst is key.

See Dalton Trans. 2011 (in press), Adv. Synth. Catal. 2009, 35, 188; Chem. Commun. 2008, 253; Helia 2007, 30, 133; J. Am. Chem. Soc. 2007, 129, 8912; Catal. Org. React. 2007, 115, 13; Organometallics 2006, 25, 2157.

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