A New Catalyst Design Methodology: Integrated Atomic-Level Modification and Intrinsic Kinetic Characterization

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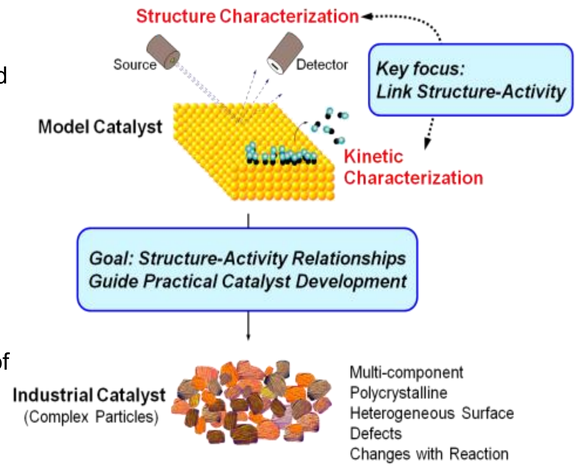
Model *vs.* Practical Catalysts

Motivation

- Practical catalyst development is hampered by a lack of fundamental information relating the surface composition of a catalyst to its kinetic performance.
- The surface is compositionally different from the bulk and may change over the course of reaction.



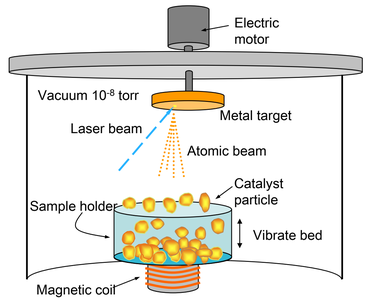
Overview

- Here we follow the evolution of Pd/SiO_2 and VPO catalysts modified using atomic beam deposition.
- Testing the SiO_2 material activity towards O_2 and CO conversion was achieved using TAP vacuum pulse response experiments, pulsed-TPR as well as normal pressure steady-state experiments.
- Testing of the modified VPO materials was achieved with TAP vacuum pulse response experiments of Butene.

Key Results

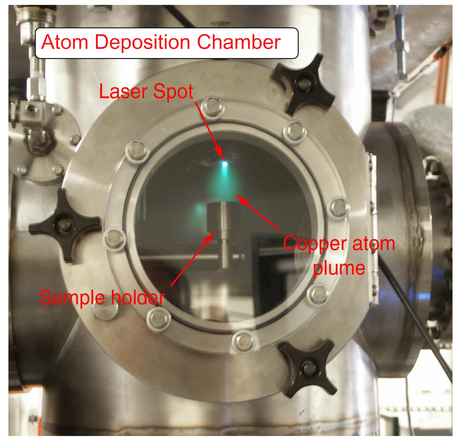
- We find that chemical probes can detect ultrasparse quantities on complex materials that are difficult to detect with structural techniques.
- Pulsed-TPR reveals an active 'self-assembly' process of metals deposited on an inert support.
- Addition of minute quantities of surface metals shows a dramatic affect on selectivity.

Pulsed Laser Atomic Beam Deposition



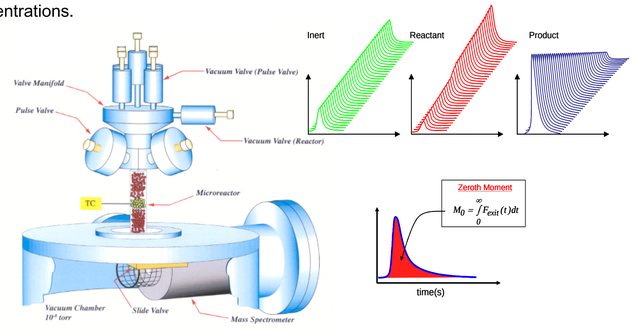
Metal atoms are produced by focusing a high-energy laser pulse on a transition metal target. Atoms ejected from the target impinge on the particle bed suspended below the target. The particle bed is continuously agitated so that the particles will be uniformly coated.

On Complex Particles…



Temporal Analysis of Products (TAP) Experiment

Measuring changes in intrinsic kinetic properties related to changes in catalyst surface concentrations.

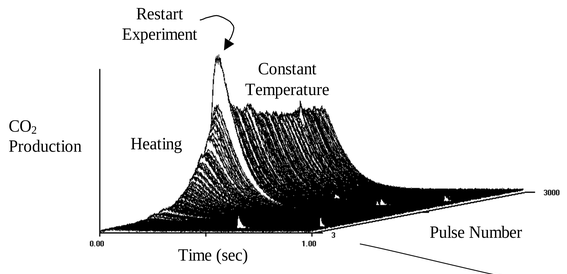


Pulsed Temperature Programmed Reaction

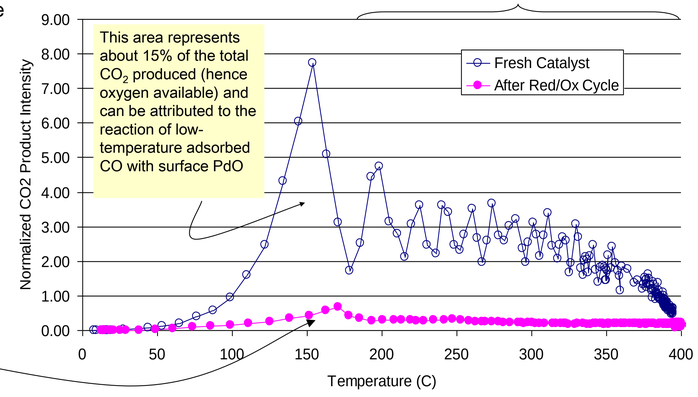
This is a unique adaptation of the traditional TPD experiment where the temperature is ramped but the reacting species concentration may be maintained at a constant value with a pulsed input.

To eliminate the native oxide layer acquired during catalyst preparation and ambient transfer the $Pd/PdO/SiO_2$ samples prepared using atomic beam deposition were exposed to a series of CO pulses while the temperature was ramped. CO_2 production occurs via reaction with a native oxide layer.

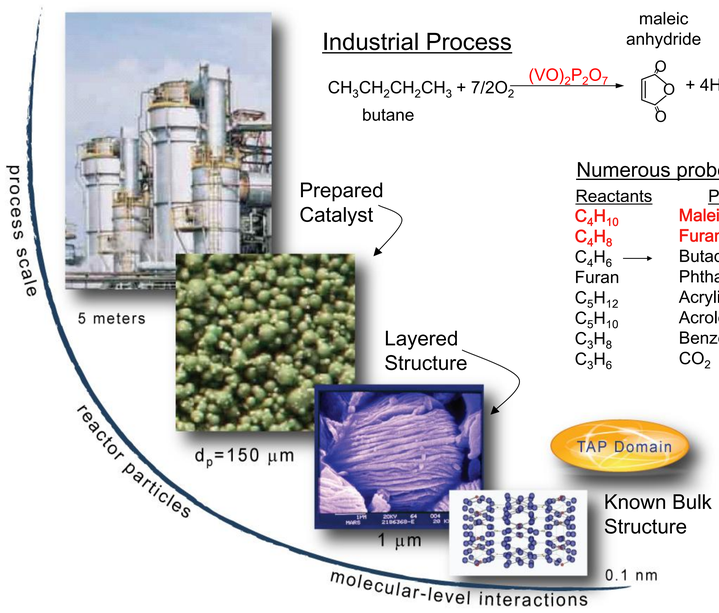
After a maximum production in CO_2 is reached, a damped oscillation in production is observed. This trend was highly reproducible on separately prepared samples and was no longer observed once the catalyst was exposed to a redox cycle.



Since the CO input is constant the oscillatory behavior in CO_2 production must arise from a changing amount of reactive oxygen.



Engineering the Active Site of an Industrial Process



Industrial Process

$CH_3CH_2CH_2CH_3 + 7/2O_2 \xrightarrow{(VO)_2P_2O_7} \text{maleic anhydride} + 4H_2O$

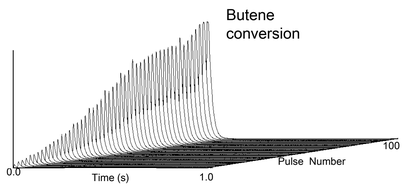
butane

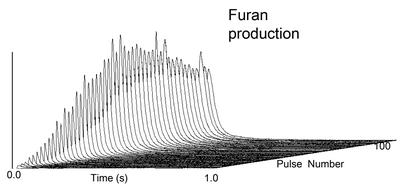
Numerous probe reactions

Reactants	Products
C_4H_{10}	Maleic anhydride
C_4H_8	Furan
C_4H_6	Butadiene
Furan	Phthalic anhydride
C_5H_{12}	Acrylic acid
C_5H_{10}	Acrolein
C_3H_8	Benzene
C_3H_6	CO_2

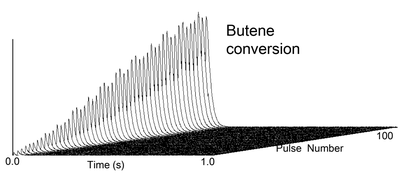
A single reactor equilibrated VPO sample was divided into smaller samples, which were used as un-promoted controls and deposition substrates. In a typical deposition experiment, 140 mg of VPO powder was loaded into the sample holder, and the deposition chamber was pumped down to $<10^{-6}$ Torr. Samples were exposed to the pulse beam for 15 minutes at a pulse rate of 10 Hz.

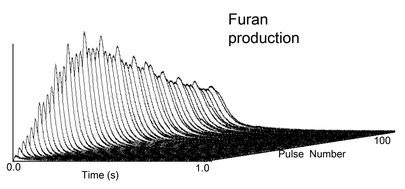
Un-promoted VPO

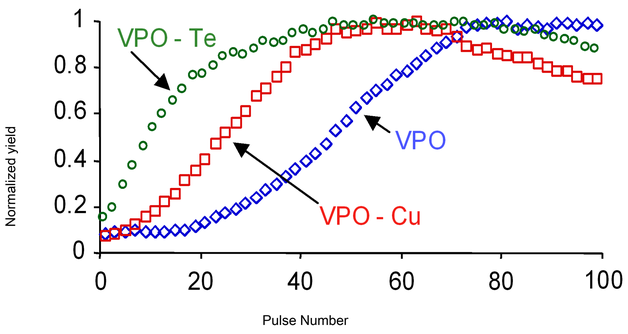




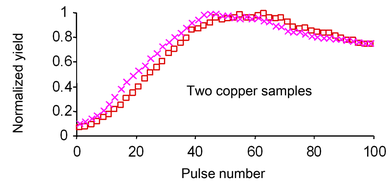
VPO - Cu deposition (Total coverage < .005 monolayers of Cu atoms)







Our initial results using reactor-equilibrated VPO as a model system indicate that the addition of relatively small amounts of metal atoms can have a dramatic effect on catalyst selectivity. With coverages below 0.05 monolayers, the copper and the tellurium modified samples exhibit different trends in furan production. In both cases, the maximum in furan yield occurs earlier in the pulse cycle than it does in the case of a reactor equilibrated sample. The difference in the behavior of the two metals may be attributed to a difference in the chemical nature of Cu and Te.



The correspondence between the curves shows that the change in furan production relative to a reactor-equilibrated sample can be attributed to the deposition of copper and that the affect can be reproduced.