Novel Catalyst Synthesis Methods (Combining TAP-2 Experiments with Atomic Beam Deposition)

Rebecca Fushimi[1], John T. Gleaves[1*], Gregory Yablonsky[1], Anne Gaffney[2], Mike Clark[2], Scott Han[2]

[1]*Department of Chemical Engineering, Washington University, One Brookings Drive, Box 1198, St. Louis, MO 63130*

[2]*Rohm and Haas Company, 100 Independence Mall West, Philadelphia, PA 19106-2399*

*klatu_00@che.wustl.edu

Introduction

It is often difficult to gather information on detailed structure-activity correlations on practical catalysts because direct observation and characterization of catalytic sites is difficult even with surface sensitive techniques. However, relating catalyst surface composition-structure to catalyst performance is an important element of a rational approach to practical catalyst development. In this presentation, we present a new approach for precisely tailoring the surface of complex catalytic particles at the atomic level. We describe a new apparatus that combines an atomic beam deposition (ABD) system with a Temporal Analysis of Products (TAP-2) reactor system. The ABD system allows us to prepare catalyst samples by directly depositing metal atoms and metal oxide clusters in sub-monolayer amounts on the surface of micron-sized particles. After deposition TAP pulse response experiments are used to precisely measure kinetic characteristics of the newly fabricated catalyst samples. The goal of combining ABD with TAP experiments is to develop a method of establishing direct, reproducible correlations between changes in catalyst surface composition and changes in its activity.

Materials and Methods

Atomic deposition under ultra-high vacuum conditions offers a precise method of delivering metal atoms to a solid surface. Our ABD system produces metal atoms by focusing the light from a pulsed excimer laser on to the surface of a metal (palladium) target. The energy from the pulse ejects a spray of atoms. Directly beneath the target sits a cylindrical sample holder, which has a magnetic diaphragm in the bottom. Sending a pulsed current through an electromagnetic coil causes the diaphragm to vibrate, and the particles to continuously move and turn over on the diaphragm surface. After deposition, samples are transferred to a TAP-2 reactor and kinetically characterized. In the TAP system, a minute amount of reactant gas (~10^{14} molecules/pulse) is pulsed into a micro-reactor. The output from the reactor outlet is measured using a quadrupole mass spectrometer. The predominant transport factor inside the reactor is Knudsen diffusion.

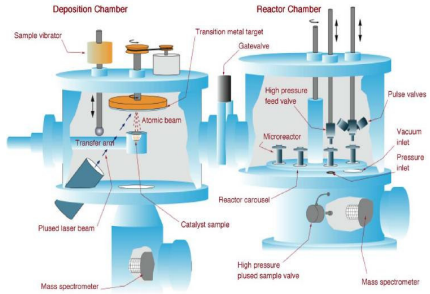

Fig. 1 Simplified schematic representation of combined TAP-2 and atom deposition system.

Results and Discussion

Laser ablation has been used extensively to deposit metals on various substrates to form a thin film. In our experiments, we deposited different loadings of Pd atoms onto 210-250 μm diameter inert quartz (SiO_2) particles. An interesting oscillatory behavior was found in the pulsed temperature-programmed reaction (TPR) of fresh Pd catalyst samples. Figure 2 shows CO_2 production as a function of temperature over a catalyst sample containing 750 Pd laser pulses. A maximum in CO_2 production is observed at 154 °C. After the maximum, CO_2 production drops rapidly as the sample continues to heat. The initial steep drop in CO_2 production is followed by a gradual decrease with periodic bursts giving the appearance of a damped oscillation. All freshly deposited samples exhibited this oscillatory behavior. The reactor temperature was maintained at 400 °C until CO_2 production was <5% of its maximum value. The trend in CO_2 production and the total amount produced was highly reproducible on separate samples prepared with identical Pd loadings. Heuristically, every peak in the dependence in Figure 2 can be viewed as a typical TPR peak related to a specific form of catalyst oxygen. CO_2 production during the first peak corresponds to the depletion of accessible surface oxygen. Then, the series of peaks that follow can be considered as resulting from reaction of CO with other forms of catalyst oxygen. Thus, abrupt changes in the amount of oxygen indicate abrupt changes in the Pd/PdO composition. The observed phenomenon can be interpreted as an example of reactive self-assembly, the combination of reaction kinetics, diffusion, and surface phase transitions. The analogous self-assembly processes in Pd catalytic systems have been reported in the literature [5].

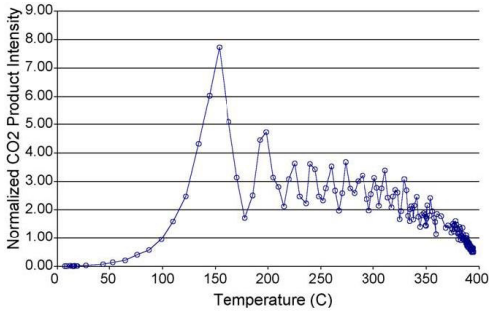

Fig. 2. CO_2 production (determined by measuring the zeroth moment of the CO_2 responses) over fresh Pd deposits (750 pulses) obtained by pulsing CO and ramping the temperature from RT to 400 °C.

Significance

The combination of the ABD system and the TAP system as a single apparatus provides a convenient way to fabricate atomic level catalysts assisted by precise kinetic characterization.

References

1. J.T Gleaves et al. *Applied Catalysis* A: *General* 160 (1997) 5548
2. S.O. Shekhtman, G.S. Yablonsky, S. Chen, J.T. Gleaves, *Chem. Eng. Sci.* 54 (1999)
3. Yablonsky, G.S, et al. *Journal of Catalysis* 216 (2003) 120-134.
4. Aggarwal, S. et al. *Science* 287 (2000) 2235-2237.