

Novel Catalyst Characterization Techniques (Isotopic Switching Demonstrated using Pump-Probe TAP-2 Experiments)

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Introduction

The application of TAP pulse response experiments to catalytic structures has been a major breakthrough in the catalyst characterization field. However, during typical transition metal catalysis, it is difficult to determine the migration of subsurface oxygen and its effect on oxidation reactions. One way to overcome these challenges is by using two distinct isotopes of oxygen; one during catalysis pretreatment and one during experimentation. By utilizing the mass differentials of the two isotopes, it is possible to distinguish between initially subsurface oxygen which has migrated to the surface and surface oxygen which is replenished in a traditional "Pump Probe" TAP pulse response experiment.

Materials and Methods

The experiment was performed using the temporal analysis of products (TAP) reactor system. TAP is a unique kinetic characterization tool that pulses in a minute amount of reactant gas through magnetically controlled pulse valves into a micro-reactor. The output is measured using a quadrupole mass spectrometer and the data is given as a series of pulse curves. One type of experiment performed using the TAP system is the pump-probe experiment. The pump-probe experiment utilizes two different pulse valves and maintains the oxidation state of the catalyst by re-supplying consumed oxygen in alternating pulses. The catalyst was fabricated using atomic beam deposition of palladium (Pd) metal atoms on inert quartz particles. The catalyst was first oxidized completely in an oxygen flow (25 cc/min diluted in argon, $^{16}\text{O}_2/\text{Ar}=0.7$) at 430 °C for 30 minutes. Then, a series of alternating CO and $^{18}\text{O}_2$ pulses of equal intensity were passed over the Pd catalyst. The temperature was lowered to 350 °C before starting the pulsing in an effort to minimize the repopulation of the surface with ^{16}O from the bulk. At time zero, the $^{18}\text{O}_2$ pulse was injected and after a delay of 0.5 second the CO pulse was injected. The delay of 0.5 seconds ensures enough time for the $^{18}\text{O}_2$ to adsorb onto the catalyst surface, the CO to find an oxygen atom to react with, and for the product, CO₂, to completely come out of the reactor outlet.

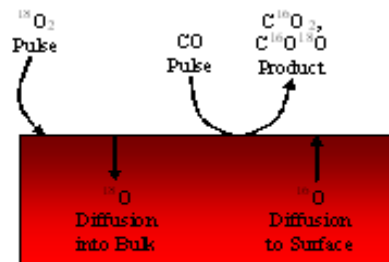


Fig 1. Schematic of isotope labeled O₂ migration and subsequent reaction.

Results and Discussion

At the beginning of the pump/probe experiment the total production of CO₂ is greatest and then decreases towards a steady level. Note that initially all CO₂ is produced via reaction with ^{16}O . Later, as more sites become available for $^{18}\text{O}_2$ adsorption the amount of CO₂ produced with either oxygen isotope become roughly equal. The initial drop in the CO₂ production indicates that the pulsed mode of oxidation can not completely repopulate the surface to the same state as is available after atmospheric oxygen flow. A small fraction of oxygen sites are left empty during the pulsing period since the rate of bulk migration is low at 350 °C and the oxygen pulse intensity is low. Rather than a chemical change in the surface, the small decrease in CO₂ production can be attributed simply to counting, i.e. the oxygen pulse is unable to sample each vacancy during its transport through the reactor. An increase in the oxygen pulse intensity would increase the number of sites replenished by the oxygen pulse and raise the production level of CO₂. These observations were confirmed when the CO pulsing was discontinued and the oxygen conversion quickly resumed the 0% conversion level seen at the beginning of the experiment.

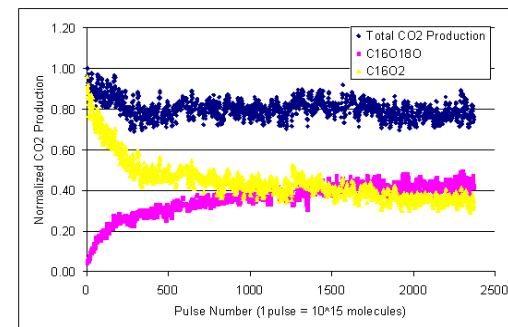


Fig 2. Zeroth moments of CO₂ production during pump/probe experiment with $^{18}\text{O}_2$ and CO over catalyst at 350 °C.

Perhaps the most significant result that can be gleaned from the data presented above is that the production of CO₂ becomes constant during the pump/probe experiment. When starting with a catalyst oxidized in an atmospheric pressure flow, oxygen removed via reaction with CO may be replaced with low pressure oxygen pulses. This indicates that the catalyst surface created under atmospheric pressure oxidation conditions can be re-established under high vacuum pulsed conditions. The total amount of oxygen available is greater when oxidizing with an atmospheric pressure flow, as shown by earlier data of CO multipulse reduction. Although the total amount of oxygen changes, the surface chemistry is the same. This is a significant conclusion and demonstrates that the pump/probe experiment is one solution to the pressure-gap concern of high vacuum kinetic studies.

Significance

We have shown a way in which we can couple TAP pulse response experiments with isotopic labeling in order to elucidate information about subsurface oxygen migration during pump probe experiments.

References

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