NEEDLE IN A HAYSTACK CATALYSIS - AN EXPERIMENTAL STUDY USING TEMPORAL ANALYSIS OF PRODUCTS (TAP)

AIChE 2008 SPRING NATIONAL MEETING

Xiaolin Zheng, Washington University in St. Louis, St. Louis, MO, USA
John T. Gleaves, Washington University in St. Louis, St. Louis, MO, USA
Gregory S. Yablonsky, Saint Louis University, St. Louis, MO, USA
Thomas Brownscombe, Shell Oil Company, Houston, TX, USA
Anne Gaffney, ABB Lummus Global, Inc., Bloomfield, NJ, USA
Mike Clark, Rohm and Haas, Spring House, PA, USA
Scott Han, Rohm and Haas, Spring House, PA, USA

Introduction

Two general experimental approaches using different forms of catalytic materials are used in heterogeneous catalysis research. The "model catalyst" approach employing materials with well-defined surfaces, such as metal single crystals, provides a direct method of linking surface structure to elementary steps in a catalytic process.

The second approach, which can be called the "practical catalyst" approach, is the basis for most industrial catalyst development. Practical catalysts include supported metals, mixed metal oxides, and zeolites. The "practical catalyst" approach involves the systematic synthesis, testing, and characterization of numerous catalyst samples. In general, practical catalysts have complex ill-defined surfaces, and the active surface structure cannot be directly identified. Also, the measurement of catalytic activity under process conditions does not provide a direct link between structure and activity. In addition, the composition of a practical catalyst can change under the influence of the reaction medium resulting in a change in its properties. Consequently, practical catalyst development is hampered by a lack of fundamental information on the composition and structure of the catalytic phase or catalytic site.

Information from model catalyst studies is intended to provide guidance in the development of practical catalytic materials. However, the application of fundamental information has not been straightforward, since there is a significant "gap" between the conditions of "real world" catalytic processes, and those of model reaction studies. Bonzel [1] was the first to discuss the problem and coined the term "pressure gap" to emphasize the 10^{12} difference in reactant pressures. Practical and model catalyst experiments are also separated by a "materials gap" arising from the differences in structural and compositional complexity of catalyst samples. The materials gap presents a significant problem since the interplay of bulk and surface and the complex interactions of different constituents in practical catalysts are not easily reducible to a set of simple individual interactions. It is questionable whether results obtained at vacuum conditions on a set of well-defined uniform surfaces can be extrapolated to practical materials operating at atmospheric pressures, unless the uniform and practical samples can be directly compared experimentally.

Reactions on practical catalysts can be performed at vacuum conditions and at atmospheric pressures using a TAP (Temporal Analysis of Products) reactor system [2, 3, 4, 5]. This paper presents new results from a series of heterogeneous CO oxidation experiments using a single micron-sized catalyst particle surrounded by non-active quartz particles ("platinum needle in quartz haystack"). The catalyst particle occupies less than 1% of the cross-sectional area of the microreactor, so that the reaction zone can be considered a point source. This construction eliminates non-uniformity in reactant concentration and catalyst composition even in the domain of high conversions. The results are significant because they allow direct comparison between transient response experiments performed at vacuum conditions and steady flow experiments performed at atmospheric pressures – bridging the “pressure gap.” Also, use of a single particle opens the door to a variety of new non-steady-state experiments that can supply intrinsic kinetic information, which can be directly related to catalyst composition and structure. For example, the single particle could be a well-defined single crystal, or an inert particle with metal deposited on the surface. Since all experiments use the same basic unit, a single particle, and the same reactor configuration and conditions, the results can be directly compared. Because TAP transient response experiments provide intrinsic kinetic data (e.g. number of active sites, site activation energy, etc.) and transport data, experiments performed on single crystals can be correlated with experiments performed on multi-crystalline materials. These experiments provide a new approach to bridging the materials gap.

Experimental

TAP Reactor

All single particle kinetic experiments were performed using a Temporal Analysis of Products (TAP-2) reactor system (Fig. 1A). The TAP-2 reactor can be used to perform TAP vacuum pulse response experiments, and atmospheric pressure steady-state, step-transient, and temperature programmed experiments [2, 3, 4, 5].

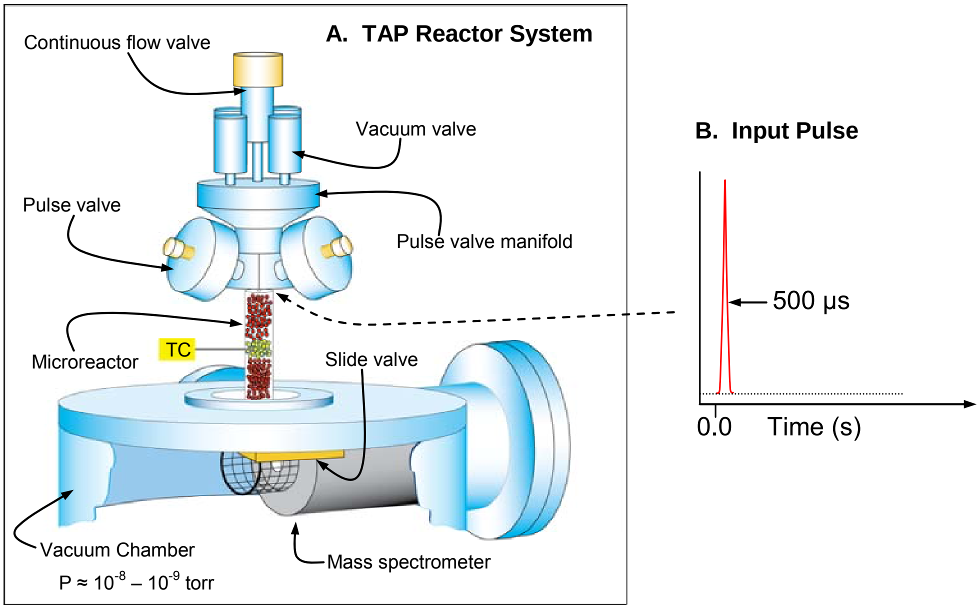

Fig. 1. (A) Schematic of TAP-2 reactor apparatus, which consists of 3 main parts: the pulse valve manifold, microreactor, and vacuum chamber containing the mass spectrometer. **(B)** Each inlet reactant pulse upon entering the microreactor is a very narrow pulse, often represented by the delta function. The pulse broadens as it travels through the microreactor, and in the case of an inert gas, the pulse shape will be the same as the standard diffusion curve.

Unlike conventional transient response experiments, TAP experiments use no carrier gas, and each pulse contains a very small amount of reactant (≈10^{-9} mol/pulse). During a pulse, the gas density in the microreactor drops rapidly and the molecular mean free path becomes greater than the distance between particles. As a result, reactant and product molecules formed during chemical reaction move among the particles randomly, and independent of one another. Gas transport through the reactor can be characterized as Knudsen diffusion, which has the property that the diffusivity of each gas in a mixture is independent of the composition of the mixture as a whole [2, 3, 4, 5]. Mathematically, a Knudsen pulse can be described using Fick's second law (diffusion equation).

In a TAP Knudsen pulse response experiment, a narrow pulse of reactant gas (Fig. 1B) is injected into a packed-bed microreactor using a high-speed pulse valve. The microreactor is a stainless steel tubular reactor with dimensions 4.19 cm long and 0.64 cm in diameter. The reactor contains an internal thermocouple and can be operated isothermally or temperature programmed. The microreactor is attached to a high-throughput vacuum chamber (10^{-8}-10^{-9} torr) containing a UTI 100C QMS mass spectrometer. A 2-position slide valve assembly separates the reactor outlet and the mass spectrometer. When the slide valve is in the closed position, the microreactor can be operated at atmospheric pressures (atmospheric flow experiments). In the open position, the reactor operates at vacuum conditions (TAP pulse response experiments) [2, 3, 4, 5].

Catalyst Configuration

In a typical experiment, the microreactor was packed with approximately 100,000 inert quartz particles (210-250 μm in diameter) and a single catalyst particle (300-400 μm in diameter) usually positioned in the center of the reactor bed (Fig. 2A). The microreactor is heated resistively, and the internal temperature adjacent to the catalyst particle is sampled with a shielded thermocouple. Results presented in this paper are for particles of platinum (Pt) metal (Fig. 2B, 2C, 2D). The catalyst particle and the inert quartz particles are nonporous so that gas diffusion or mass transfer within particles does not occur.

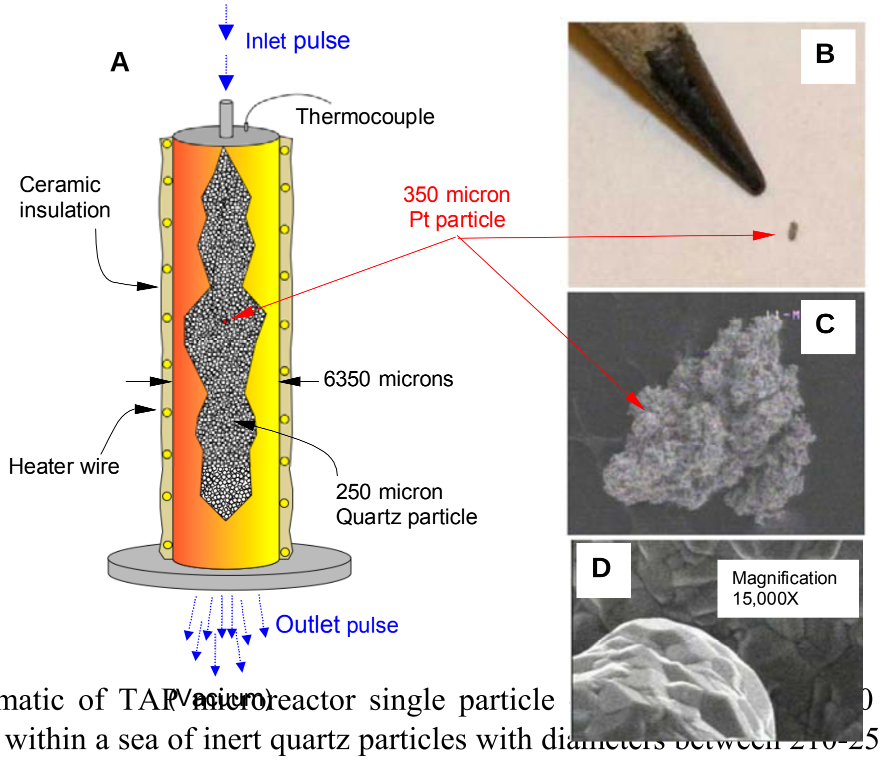

Fig. 2. (A) Schematic of TAP microreactor single particle 0 μm diameter Pt particle is packed within a sea of inert quartz particles with diameters between 210-250 μm. There are

approximately 100,000 inert particles and only 1 active particle in the entire microreactor volume. **(B)** Actual image of single particle Pt polycrystalline catalyst taken with a digital camera. The image compares the Pt particle to a pencil point to demonstrate the actual size of the catalyst particle. **(C)** SEM images showing the entire polycrystalline Pt particle. The diameter of the particle is estimated to be 350 μm. **(D)** Inset gives high magnification (15,000X) SEM image of Pt particle surface, which shows the surface is nonporous.

Results and Discussion

CO Oxidation on Pt Particle under TAP Vacuum Conditions

CO oxidation pulse response experiments were performed using the TAP "pump-probe" format. Mixtures of O_2/Ar (70/30) and CO/Ar (70/30) stored in separate pulse valves were injected into the microreactor forming a train of alternating pulses of O_2 and CO. In TAP experiments, argon is typically mixed with the reactant gases to act as a reference. Because it is inert, its transient response depends only on the transport process. It is used as a measuring stick to calculate diffusivities, conversion, and kinetic parameters. The pump-probe format maintains a relatively steady oxygen concentration on the catalyst by re-supplying any consumed oxygen in alternating O_2 pulses. In single Pt particle experiments, CO conversion was constant during multi-pulse pump-probe experiments at a steady reactor temperature. Therefore, based on experimental evidence, it can be stated that the oxygen coverage on the Pt particle is restored to the same value prior to each CO pulse.

In a pump-probe experiment [2, 3], the separation time between reactant pulses can be varied. Time delay between the reactant pulses can be changed to investigate the effects of changes in the surface lifetime of reactive adspecies on the dynamics of catalyst surface processes. In the experiments plotted in Figure 3, the O_2 and CO pulses were evenly spaced and separated by a time delay of 2 seconds. Identical experiments using time delays of 1 and 3 seconds were also performed, and no difference in the amount of CO_2 produced was observed. This indicates that the surface oxygen storage is approximately constant within the pump-probe time delays.

The amount of CO_2 produced in the pump-probe transient response experiment (Fig. 3A, 3C) can be determined by measuring the area (zeroth moment) under the transient response curve [6]. To determine CO_2 yield, the zeroth moment is normalized relative to the amount of CO in a single pulse. The absolute amounts of O_2, CO, and CO_2 are determined by comparing the response obtained in a reaction with one obtained using a standard blend. All responses are compared to the Ar response, which is the internal reference.

The black plot (Fig. 3C) represents the total CO_2 yield during one pump-probe cycle. The red and blue plots (Fig. 3C) show the CO_2 yield for O_2 and CO pulses respectively. The striking feature of these dependences is the high CO_2 yield that is achieved despite the catalyst particle occupies less than 0.1% of the total reactor volume. At 170 ºC, the yield for the individual O_2 and CO pulses reach a maximum, making the total yield equal to approximately 95% during one pump-probe cycle. This means that under Knudsen diffusion conditions, at least 95% of the CO molecules pulsed into the reactor must strike the particle.

Above 170 ºC, the CO2 yield decreases, more rapidly for the O_2 pulse than the CO pulse. From 170 to 350 ºC, the CO_2 yield on the O_2 pulse decreases from a maximum of 52% to < 5%. In the same interval, the yield on the CO pulse decreases from 43% to 25%, so that the overall yield drops from 95% to less than 30%.

The difference between CO_2 dependences obtained in O_2 and CO pulse experiments can be explained within the modified adsorption mechanism (Langmuir-Hinshelwood mechanism). During the O_2 pulse, adsorbed oxygen may react with adsorbed CO molecules which are likely isolated at the reaction temperatures. In contrast, during the CO pulse, the adsorbed CO molecule may interact with different forms of stored oxygen, e.g. via the gradual destruction of the surface oxygen structure (surface phase islands). In this case, the CO_2 yield decreases not as rapidly. However, there is a general feature to both dependences. The yield peak ("turning point") occurs at the same temperature of 170 ºC for both CO and O_2 pulses. Based on the adsorption mechanism, it is reasonable to assume that it is the point of transition from a CO dominated catalyst surface (below 170 ºC) to an O_2 dominated catalyst surface (above 170 ºC).

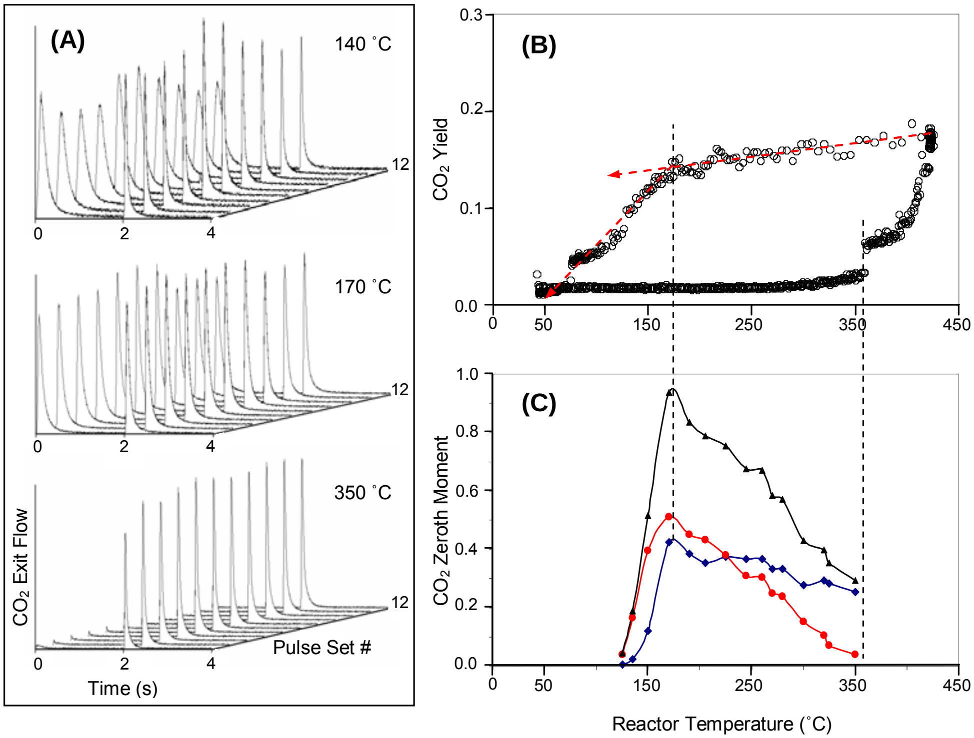

Fig. 3. Comparison of CO_2 produced during TAP vacuum pump-probe experiments and atmospheric flow experiments for CO oxidation over single Pt particle with the same composition of reactants. **(A)** A typical set of pump-probe CO_2 responses (m/e = 44) for reaction at 140, 170, and 350 ˚C. **(B)** CO_2 production observed from atmospheric flow experiment. The CO_2 produced while increasing reactor temperature is less than the CO_2 produced during reactor temperature decrease as shown by the counter-clockwise hysteresis loop. **(C)** CO_2 production observed from vacuum pump-probe experiment. The black line (-▲-) represents the total CO_2 yield. The red (-●-) and blue lines (-♦-) represent the CO_2 yield on the O_2 pulse and CO pulse, respectively.

CO Oxidation Experiments at Atmospheric Pressures

After completing the set of vacuum pulse response experiments, the slide valve was closed so that the reactor could be operated at atmospheric pressures. Prior to introducing an O_2/CO mixture, the particle bed was exposed to a hydrogen flow (20 cc/min diluted in Ar, H_2/Ar = 1) at 350 ˚C for 1 hour. The H_2 flow was used to remove any memory of the previous pump-probe experiments. The reactor was then cooled and a total flow of 50 cc/min of O_2, CO, and Ar (O_2/CO/Ar = 1) was introduced through the continuous valve, giving a gas residence time in the reactor of 1.8 s. Conversion under atmospheric conditions was quite high despite the short contact residence time inside the reactor (Fig. 3B).

The temperature dependence of CO_2 production was obtained by heating or cooling the reactor at a constant rate while maintaining an input flow of 50 cc/min. The internal reactor temperature was ramped from 40 ˚C to 430 ˚C over a 40 minute interval. Upon reaching 430 ˚C, the reactor temperature was held constant for 5 minutes and then decreased at the same ramp rate to room temperature.

During atmospheric pressure experiments, a small amount of the reactor effluent was diverted into the mass spectrometer chamber, and its mass spectrum was continuously monitored. The temperature dependence of the CO_2 yield is characterized by two branches, which form a counter-clockwise hysteresis loop (Fig. 3B). The lower branch occurs during the up ramp and the upper branch during the down ramp. On the lower branch of the hysteresis loop, at approximately 350 ˚C, a dramatic rise in CO_2 yield is observed. On the upper branch of the hysteresis loop, a maximum in CO_2 production of 20% is observed at 430 ˚C. At the temperature of approximately 170 ˚C ("turning point"), a significant decrease in CO_2 occurs.

The phenomenon of yield hysteresis is well known in heterogeneous catalysis, particularly in the heterogeneous CO oxidation reaction over noble metals [7]. Such behavior is also explained based on the adsorption mechanism in which O_2 and CO compete for active catalytic sites on the metal surface. From this point of view, the "turning point" is the temperature at which O_2 domination on the Pt surface is changed by the CO domination of the catalyst.

Comparison of Results from Vacuum and Atmospheric Pressure Regimes

Both vacuum and atmospheric pressure data exhibit several striking features. Perhaps most surprising is the very high conversion observed in TAP pulse response experiments. Despite the fact that the Pt particle occupies less than 0.1% of the total reactor volume, it is struck by at least 95 out of 100 CO molecules pulsed into the reactor.

In a TAP pulse response experiment, gas molecules move independently, primarily colliding with particles and the reactor walls. On average, a CO molecule experiences between 100,000 to 500,000 collisions before it exits the microreactor [8]. As a result, a molecule that initially bypasses the Pt particle can reverse its direction during its next collision and return to the Pt particle.

Conversion in atmospheric pressure experiments is also quite high. The residence time in the microreactor is longer than in a TAP experiment, but the apparent contact residence time in the reaction zone is about 2 orders of magnitude less. Nevertheless, CO conversion reaches 20%. Clearly, the real residence time in the reaction zone is larger, and mixing is also significant in atmospheric flow experiments.

An essential requirement for obtaining precise kinetic data is uniformity within the reaction zone in the reactant concentration profile and catalyst composition. The reactant concentration can be defined as uniform if its spatial difference is small compared to its maximum value. In single particle experiments the reaction zone is the particle surface. In vacuum pulse response experiments the reaction zone samples the entire reactor volume, and our estimates show that non-uniformity is negligible [9]. In atmospheric pressure experiments the reaction zone samples an area at least 67 times larger than the particle. Consequently, in both experiments non-uniformity is negligible, so it can be assumed the reaction zone is perfectly mixed.

Pulse response data obtained in high vacuum experiments can be used for direct determination of the number of active sites or storage of an active component [3, 10]. For a single particle, this number is comparable with the number of moles in a pulse, and can be determined in a single experiment. Data from TAP pulse response experiments can also provide details related to the steps in a complex reaction, i.e. kinetic coefficients of different reactions (reactant adsorption, interaction of reactants with other pre-adsorbed reactants), energies of activation and pre-exponential factors, and the dependence of all these parameters on the catalyst pre-treatment [3, 4, 10].

Conclusions

The new TAP reactor configuration, the single particle configuration, has demonstrated the high sensitivity of the TAP reactor and the ability to compare kinetic characteristics of the same catalyst under both high vacuum and atmospheric pressures. Experiments performed under vacuum and atmospheric pressures exhibit a "turning point" at 170 ˚C, which indicates a transition from the O2 dominating regime to the CO dominating regime (or vice versa) on the Pt single particle. In both cases, the "turning point" temperature is about the same at 170 ˚C. Therefore, the "turning point" temperature is the pressure independent characteristic which is governed by the steps of the complex catalytic processes with no participation of gas reactants or products (e.g. CO desorption, interaction between adsorbed oxygen and CO). The fact of observation of such pressure independent characteristic creates a new possibility for bridging across the pressure gap [11].

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