

CO Oxidation on Rh/SiO₂ and Pt/SiO₂ Model Catalysts at Elevated (~10torr) Pressures

Matthew Lundwall, Sean M. McClure, Fan Yang, Zihao Zhou, D. Wayne Goodman*
Texas A & M University, College Station, TX 77842 (USA)
*goodman@mail.chem.tamu.edu

Introduction

For almost 100 years, CO oxidation has been intensively studied on Pt-group metals [1]. The reaction is known to occur through a Langmuir-Hinshelwood mechanism by which CO and O₂ must co-adsorb prior to reaction. Recently, this view has been challenged as various oxide phases have been proposed to exist on Pt-group surfaces under reaction conditions [2]. Studies on metallic particles indicate size dependence for oxidation [3,4]. Of concern is what conditions CO oxidation kinetics on single crystals can be translated to technical catalysts. To address this issue, we prepare and characterize Rh/SiO₂ and Pt/SiO₂ model catalysts in ultra high vacuum (UHV) and transfer the samples in-situ to a high pressure cell where CO oxidation reactions are performed. CO oxidation reactions are also performed on Rh(111) and Pt(110) in the same apparatus for direct comparison. Estimates of surface active-sites and size estimates from desorption experiments and reaction studies are determined and compared with results from scanning tunneling microscopy (STM) measurements of particles grown on SiO₂ thin (0.3nm) films.

Materials and Methods

Model catalyst samples were prepared in UHV on a Mo(112) single crystal. SiO₂ films (~1.5 nm) were prepared by Si vapor deposition in O₂ ambient. Rh or Pt was subsequently vapor deposited to desired coverage (θ_{Rh}) based on Auger calibration. CO binding and desorption characteristics were obtained from infrared reflection absorption spectroscopy (IRAS) (fig.1) and temperature programmed desorption (TPD) on particles along with measurements obtained on a Rh(111) and Pt(110) single crystal for direct comparison. After characterization in UHV, samples were transferred *in-situ* to a contiguous high pressure cell (~0.3L). CO oxidation reactions (P~8 Torr) were conducted in a batch reactor mode using O₂/CO ratio gas mixtures from (1/10)-(2/1) on various Rh, Pt coverages. CO₂ formation rates were determined from the first 10% of reaction by $\frac{1}{2} dP_{CO_2}/dt = dP_T/dt$. Reaction rates on Rh(111) and Pt(110) were also obtained in the same set-up for direct comparison. STM measurements were conducted in a separate UHV system where ultra-thin silica films (~0.3nm) were prepared by vapor deposition of 1ML Si on a pre-oxidized Mo(112) surface, followed by annealing in O₂. Rh or Pt particles were subsequently deposited and imaged at T=300 K under UHV conditions.

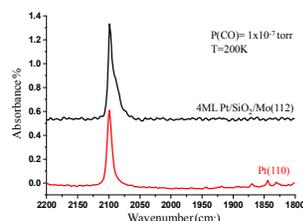


Figure 1: CO-IRAS of 4ML Pt/SiO₂/Mo(112) and Pt(110) in 1x10⁻⁷torr CO at 200K

Results and Discussion

Reactivity measurements on Rh/SiO₂ (Fig 2) and Pt/SiO₂ (not shown) exhibit activation energies comparable to Rh(111) and Pt(110) (E~100-120kJ/mol). Normalization of particle to single crystal reaction data coupled with AES and TPD measurements provide an estimate of active-sites as a function of θ_{Rh} (Fig. 3, red circles). Active site estimates based on STM images of Rh/SiO₂ films (Fig. 3, blue triangles) display similar site trends. Results indicate an apparent structure insensitivity for CO oxidation on Pt and Rh particles under the present CO dominant conditions, consistent with previous single crystal and technical catalysts.

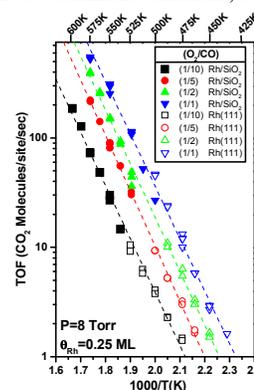


Figure 2: CO₂ reaction rate (TOF) vs. 1000/T(K) performed for various O₂/CO ratios over θ_{Rh} ~0.25ML Rh/SiO₂ and Rh(111) [5]

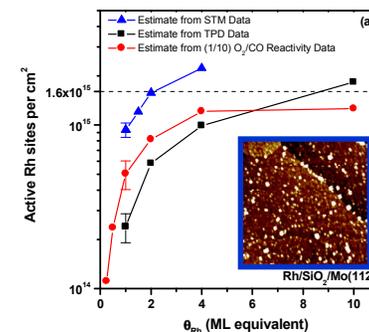


Figure 3: Active Rh sites per cm² vs. θ_{Rh} as estimated from TPD (■), (1/10) reactivity data (●), and STM data (▲). Inset: STM 1ML Rh/SiO₂ 50x50nm [5]

Significance

CO oxidation kinetics on Rh and Pt show independence from electronic or structure variations associated with particle size under the present conditions. The apparent insensitivity for this reaction allows complete translation of previous results on Rh and Pt single crystals to technical catalysts. The implication of this research is two-fold: bridging the materials gap between model and technical surfaces and providing a unique method for estimating surface active-sites on solid-state Rh and Pt catalysts.

References

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