



Microkinetic modeling of H₂SO₄ formation on Pt based diesel oxidation catalysts



Hom N. Sharma*, Yunwei Sun, Elizabeth A. Glascoe

Lawrence Livermore National Laboratory, 7000 East Ave., Livermore, CA, 94550, United States

ARTICLE INFO

Article history:

Received 25 May 2017

Received in revised form 26 July 2017

Accepted 6 August 2017

Available online 10 August 2017

Keywords:

Pt catalyst

Sulfuric acid poisoning

Diesel oxidation catalyst

Sulfur oxides

Microkinetic modeling

ABSTRACT

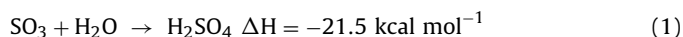
The presence of water vapor and sulfur oxides in diesel engine exhaust leads to the formation of sulfuric acid (H₂SO₄), which severely impacts the performance of Pt/Pd based emissions aftertreatment catalysts. In this study, a microkinetic model is developed to investigate the reaction pathways of H₂SO₄ formation on Pt based diesel oxidation catalysts (DOCs). The microkinetic model consists of 14 elementary step reactions (7 reversible pairs) and yields prediction in excellent agreement with data obtained from experiments at practically relevant sulfur oxides environment in engine exhaust. The model simulation utilizing a steady-state plug flow reactor demonstrates that it matches experimental data in both kinetically and thermodynamically controlled regions. Results clearly show the negative impact of SO₃ on the SO₂ oxidation light-off temperature, consistent with experimental observations. A reaction pathway analysis shows that the primary pathway of sulfuric acid formation on Pt surface involves SO₂^{*} oxidation to form SO₃^{*} with the subsequent interaction of SO₃^{*} with H₂O^{*} to form H₂SO₄^{*}.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Sulfuric acid (H₂SO₄) formation is a detrimental, yet prevalent reaction due to interactions of sulfur oxides and water on current state-of-the-art Pt/Pd based diesel oxidation catalysts (DOC) [1–3]. Once formed, H₂SO₄ poisons the DOC, increases particulate matter (PM) formation in the engine exhaust, and creates environmental problems such as acid rain formation [1,2,4]. In addition, it is detrimental to aftertreatment units in diesel engine exhaust systems, such as the selective catalytic reduction (SCR), the lean-NO_x trap, and the continuously regenerating trap (CRT) [5]. Formation of H₂SO₄ has been attributed to the oxidation pathways of sulfur in diesel fuel and lubricants (i.e., oxidation to SO₂ in the engine and further oxidation to SO₃ at the DOC due to the excess oxygen (~12%) in the exhaust). Presence of excess water vapor (up to ~7%) accelerates H₂SO₄ formation in the engine exhaust [1,3,6]. In spite of low concentrations (~1 ppm) of sulfur oxides (SO_x) in diesel engine exhaust, due to the use of ultra-low sulfur diesel fuel mandated by the U.S. Environmental Protection Agency regulations, formation of H₂SO₄ is still observed. Understanding the reaction kinetics and pathways of H₂SO₄ formation is required for a robust design and development of sulfur resistant emission aftertreatment catalysts.

Thermodynamically, formation of H₂SO₄ is exothermic; the overall reaction equation and corresponding enthalpy [7] are:



Prior studies suggest that the formation of SO₃ is extremely fast and highly favored on Pt. The SO₃ then interacts with metal or metal oxide catalysts leading to the formation of catalytically non-active metal sulfates [6,8,9]. The large binding strength of SO₃ on Pt or oxidized-Pd surfaces is one of the descriptors for the sulfation of DOC [9]. Thus, the SO₃-metal reactions eliminate the active sites of DOC from further reactions. Hence, for a complex system involving H₂O, oxygen, and sulfur oxides the reaction mechanisms and pathways are not fully understood.

Earlier experimental and modeling studies indicate that the reaction of SO₃ and H₂O is the primary route for H₂SO₄ production [10–13]. For example, in the fuel lean condition, as experienced by the DOC, oxidation of sulfur oxides is the favored path and a precursor step for the H₂SO₄ aerosol generation [14]. Phillips et al. discovered a SO₃-H₂O complex in the gas phase using microwave spectroscopy [10]. Lovejoy et al. demonstrated that the rate of H₂SO₄ formation is influenced by H₂O concentration [11]. DFT-based predictions showed a decrease in the activation energy for the reaction of SO₃ and H₂O with an increase in water coverage on the Pd(111) surface. On the other hand, in an ab-initio method based the electro-oxidation study of SO₂ on Pt(111), Kriek et al. [15] proposed H₂SO₄ formation via the HSO₃ pathway in addition

* Corresponding author.

E-mail address: sharma11@llnl.gov (H.N. Sharma).

to the SO₃ pathway. Unfortunately, prior kinetic modeling has been limited to SO₂ oxidation resulting in SO₃ formation [6,12,13,16]. Clearly the presence of H₂O in the exhaust makes the SO_x surface chemistry complex. Since complete removal of the sulfur from the fuel and lubricants is not economically viable, understanding the SO_x and H₂O chemistry in the DOCs and other systems is crucial to the development of a mitigation strategy and requires an immediate attention.

In this study, a microkinetic model is developed for H₂SO₄ formation on Pt surface that includes oxidation and H₂O interaction of sulfur oxides (SO₂ and SO₃). A microkinetic modeling approach allows us to calculate the catalytic rates, conversion, and selectivity under a given set of conditions without *a priori* assumptions of rate limiting steps or the most abundant reaction intermediate (MARI). Previously developed SO₂ oxidation microkinetic model [6,8] on Pt is extended to include SO₃ and H₂O interactions and develop a detailed understanding of the reaction pathways en route to the sulfuric acid formation. Furthermore, the analysis of HSO₃ route of H₂SO₄ formation proposed by Kriek et al. [15] shows that the pathway is not favorable under DOC conditions. The model agrees well with experimental results generated under practically relevant DOC conditions such as low emissions concentrations (ppm level), high flow rate, and high oxygen and/or water concentrations.

2. Microkinetic model

2.1. Mechanism development

The reduced surface reaction mechanism for SO₂ oxidation was adapted from previous work [6,8]. The reaction mechanism was extended to include H₂O interaction with SO_x to form H₂SO₄. In this analysis, several reactions were found to have no effect on the overall reaction progress. These eliminated reactions and the reasons for eliminating them are discussed here.

In the literature [5,15,17,18] there are two proposed pathways (i.e., Path A and Path B) involving either an SO₃* or an HSO₃* intermediate as shown below. Here, * indicates a vacant site; whereas the superscript * indicates an adsorbed species.

Path A:



Path B:



Using the Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) method [19,20] (see Appendix A), activation energies were computed for Paths A and B in the highly oxidizing environment and in the temperature range (<400 °C) of interest in this study. Our analysis showed that the activation barrier for HSO₃ formation in Path B (Eq. (4)) is too high ($E_a = \sim 33 \text{ kcal mol}^{-1}$ at 300 K) to compete with the SO₃ formation in Path A (Eq. (2), $E_a = \sim 22 \text{ kcal mol}^{-1}$). Thus, inclusion of Path B has no effect on the mechanism performance for the temperature range and emissions exhaust conditions considered here. Furthermore, no evidence of formation of HSO₃ and H₂ (possibly via $\text{OH}^* \rightarrow \text{H}^* + \text{O}^*$ or $\text{H}_2\text{O}^* \rightarrow \text{OH}^* + \text{H}^*$ to form H* species and via $2\text{H}^* \rightarrow \text{H}_2 + 2^*$ to form H₂) was reported during experiments conducted under practically relevant conditions [21]. It is noted that if the elevated temperature operation and environments differ significantly from the DOC operating conditions, the reactions in Path B may need to be considered.

Analysis showed that the reaction for water dissociation using oxygen ($\text{H}_2\text{O}^* + \text{O}^* \rightarrow 2\text{OH}^*$) reaction is feasible (activation energy,

$E_a = 9.2 \text{ kcal mol}^{-1}$ at 300 K [22]) in the temperature range studied. However, our work here indicates that this reaction also has no effect on the overall model performance. Therefore, these reactions are not included in the final proposed mechanism.

The reactions that were considered in this mechanism are chosen based on the reactants, possible intermediates, products, and the experimentally observed/proposed pathways [10,15]. Initially, the following seven surface species in the mechanism were considered: SO₂*, SO₃*, O*, H₂O*, OH*, HSO₃*, and H₂SO₄*. Adsorption/desorption steps of gas phase species (i.e., O₂, SO₂, SO₃, H₂O, and H₂SO₄) and surface reactions for SO₂ oxidation and SO₃ hydration were considered. The proposed final reaction mechanism consists of 14 elementary steps (7 reversible) reactions as listed in Table 1.

2.2. Parameter estimation

Kinetic parameters such as sticking coefficients, pre-exponential factors, binding energies, and activation energies for the elementary step reactions were estimated/extracted using a combined approach, i.e., extraction from surface science experiments in literature, estimation using the semi-empirical UBI-QEP method [19,20], or estimation from the first principles quantum mechanical Density Functional Theory (DFT) calculations [8]. Sticking coefficients for the adsorption reactions were taken from values reported in literature, otherwise the initial estimate was taken as unity. Pre-exponential factors were taken as initial estimates based on Transition State Theory (TST), e.g., 10^{13} s^{-1} for desorption and 10^{11} s^{-1} for Langmuir–Hinshelwood type surface reactions [23]. For SO₂ oxidation reaction, DFT estimates of forward and backward pre-exponential factors from our previous study were used [8]. A site density (σ) of $1.5 \times 10^{15} \text{ sites cm}^{-2}$ ($2.5 \times 10^{-9} \text{ mol cm}^{-2}$) was used in our simulations based on the estimate that Pt(111) is the most stable facet [22]. Species binding energies were based on experimental or DFT values from our previous study [8] and this work. The binding energies of HSO₃ and H₂SO₄ on Pt (111) were estimated in this work using DFT implemented in VASP [24,25] (see Appendix A for details). Binding energies are coverage (θ) and temperature (T) dependent, as shown in Eq. (6). This formalism was introduced to ensure thermodynamic consistency in a surface reaction mechanism with respect to the gas phase thermodynamics

$$Q(T) = Q(T_0) - \alpha\theta - \gamma R(T - T_0) \quad (6)$$

Here, α is the coverage dependence coefficient ($\text{kcal mol}^{-1} \text{ ML}^{-1}$), θ is the coverage of species (ML), γ is the temperature dependence coefficient for binding energies (unitless) calculated based on statistical mechanics, R is the universal gas constant ($\text{kcal mol}^{-1} \text{ K}^{-1}$), and T is the temperature (K). T_0 is taken as 300 K. Coverage and temperature dependent activation energies were calculated on-the-fly using the UBI-QEP method. Details of the α , γ , and UBI-QEP based activation energy calculations can be found in our previous papers [6,8,22].

2.3. Reactor modeling

Steady state isothermal plug flow reactor (PFR) modeling was used to simulate the monolith scale experiments conducted in various operating conditions [12,21]. The oxidation of dilute concentrations of exhaust emission gases (i.e., ppm levels) generates very little heat, thus the isothermal assumption is reasonable and justified. The governing equations for steady state PFR are given as:

Mass balance:

$$\frac{dY_k}{dz} = \frac{G_k M_k}{\rho \mu} + \left(\frac{A_c}{V_R} \right) \frac{S_k M_k}{\rho \mu} \quad \forall k = 1, \dots, n_{\text{gas}} \quad (7)$$

Download English Version:

<https://daneshyari.com/en/article/6453612>

Download Persian Version:

<https://daneshyari.com/article/6453612>

[Daneshyari.com](https://daneshyari.com)