



Water shifts PdO-catalyzed lean methane combustion to Pt-catalyzed rich combustion in Pd–Pt catalysts: In situ X-ray absorption spectroscopy



Hanieh Nassiri^a, Kee-Eun Lee^{b,c}, Yongfeng Hu^c, Robert E. Hayes^a, Robert W.J. Scott^{b,*}, Natalia Semagina^{a,*}

^a Department of Chemical and Materials Engineering, University of Alberta, 9211 – 116 St., Edmonton, AB T6G 1H9, Canada

^b Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, SK S7N 5C9, Canada

^c Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon, SK S7N 2V3, Canada

ARTICLE INFO

Article history:

Received 15 March 2017

Revised 3 June 2017

Accepted 6 June 2017

Available online 19 July 2017

Keywords:

Methane combustion

XAS

XANES

EXAFS

In situ spectroscopy

Water poisoning

Palladium hydroxide

Mechanism

Stoichiometric combustion

NGV

ABSTRACT

The addition of platinum to palladium is known to provide bimetallic catalysts that are relatively active in lean methane combustion in the presence of water at temperatures below 773 K, which is of practical interest for exhaust treatment from natural gas vehicles. The study provides insight into the wet lean methane combustion mechanism on the Pd–Pt/Al₂O₃ catalyst via in situ X-ray absorption spectroscopy studies at temperatures 473–873 K. The presence of water leads to an increased fraction of metallic Pd due to the lack of surface oxygen. The fraction of metallic Pd drops as the temperature increases. Oxygen deficit results in Pt atoms available for methane dissociation, which does not occur in the dry methane-lean feed, in which oxygen poisons Pt.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Nature's way to extinguish fires with rain, blocking oxygen access to combustible material, manifests itself similarly in flameless catalytic combustion. The current work deals with Pd-containing catalysts used for lean methane combustion in a wet atmosphere at temperatures of 300–500 °C, which occur in catalytic converters aimed at reducing methane emissions from natural-gas-fueled vehicles (NGV). When water is present in the feed, the activity of supported Pd catalysts decreases at temperatures below 450 °C [1–8], which has been explained either by the formation of inactive Pd(OH)₂ [4,9–15] or by hydroxyl/water accumulation on the support, which hinders oxygen mobility and exchange and impedes combustion [16,17].

One of the ways to diminish the negative effect of water is to introduce a platinum promoter [2,3,18], which is also used commercially in automotive three-way catalysts to oxidize CO and

hydrocarbons in the exhaust. Compared with monometallic Pd catalysts, the activity loss of Pd–Pt bimetallic catalysts in the presence of water is less severe [2,19–21]. Ex situ catalyst characterization techniques have mostly been reported, with no mechanistic studies of the water effect on the Pd–Pt catalysts at temperatures of practical interest (300–500 °C). In situ infrared spectroscopy has indicated that lower hydroxyl concentrations are present on the supported Pd–Pt catalysts than on Pd, but the analyses were performed at 200 °C [20]. It was suggested that the Pd–Pt catalyst is less affected by hydroxyl formation because it has other ways of methane activation than on PdO [20]. In a study of alternated CH₄ lean combustion/CH₄-reducing wet pulses over Pd–Pt catalysts, the difference between Pd and bimetallic catalysts was attributed to the likely ability of metallic Pt to activate methane under net reducing conditions, which was suppressed under net oxidizing conditions [18]. The effect of water presence, however, was not evaluated.

The current study investigates the effect of water in the feed on Pd and Pt species in a bimetallic Pd–Pt/Al₂O₃ catalyst during lean methane combustion by means of in situ X-ray absorption spectroscopy (XAS). It suggests a mechanism by which the bimetallic

* Corresponding authors.

E-mail addresses: robert.scott@usask.ca (R.W.J. Scott), semagina@ualberta.ca (N. Semagina).

catalyst shows an improved performance in the wet feed compared with the monometallic Pd under practically relevant temperatures (300–500 °C).

2. Experimental methods

A detailed description of the materials and catalyst syntheses can be found in our earlier work [22]. Pd nanoparticles were synthesized from palladium acetate in a colloidal dispersion in the presence of poly-N-vinylpyrrolidone using an alcohol-reduction method. Pt nanoparticles were prepared similarly from hexachloroplatinic (IV) acid. Bimetallic Pd–Pt nanoparticles were synthesized by co-reduction of the metal precursors with Pd:Pt molar ratios of 2:1. The nanoparticles were deposited on γ -Al₂O₃, followed by calcination in air at 550 °C for 16 h. Final metal loadings were determined by neutron activation analysis (NAA). CO chemisorption was performed on the catalysts after reduction, as described earlier [22]. For the calculation of dispersion and active particle diameter (hemisphere), stoichiometric factors for CO adsorption were assumed to be 0.66 for Pd to account for the linear and bridged adsorption [23] and 1 for CO:Pt.

In situ XAS measurements were conducted at the Canadian Light Source for the Pd K-edge and Pt L₃-edge on the HXMA (hard X-ray micro analysis) beamline. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were performed. The detailed description and photographs of the catalyst sample holder and the setup for the in situ analysis can be found in our earlier publication [22]. For reference compounds, Pd and Pt foils, Pd(OH)₂ (palladium hydroxide on carbon, 20 wt.% loading, Sigma-Aldrich) and PdO (99.97% trace metal basis, Sigma-Aldrich) were analyzed. To evaluate the change in Pd/PdO speciation, the calcined Pd-containing catalysts were reduced at 350 °C for 2 h in H₂ before the in situ XANES temperature-programmed analysis, unless stated otherwise. For methane oxidation under dry conditions, 0.1% CH₄ in N₂ and compressed air (ultra-zero-level, <2 ppm H₂O) were combined. In the case of wet conditions, bubblers were connected to the compressed air to produce saturated water vapor, which corresponds to 2.3 vol.% water in the feed. For dry and wet air conditions, the samples were incrementally heated from 200 to 600 °C under a flow of methane and air. The sample was held at each temperature for 30 min while measurements were taken. The flow rates of CH₄/N₂ and compressed air used were 154 and 103 mL/min, respectively. Linear combination fitting of normalized XANES $\mu(E)$ spectra was performed with the Athena program, using Pd foil, PdO, and Pd(OH)₂ standards. The software package IFEFFIT was used for data processing [24]. The EXAFS fitting was performed in *k*-space between 2 and 14 Å⁻¹ and in *R*-space between 1.2 and 3.0 Å for the Pd-edge using theoretical phase-shifts and amplitudes generated by FEFF. Face-centered cubic (fcc) bulk lattice parameters (i.e., first shell coordination numbers of 12) were used to determine the amplitude reduction factor, *S*₀², for Pd (0.93) by analyzing Pd reference foil. A homogeneous Pd–Pt alloy model for FEFF fitting was constructed based on bulk Pd–Pt lattice parameters.

Catalytic performance in the methane combustion reaction was evaluated in a tubular reactor at atmospheric pressure with online GC analysis, as described previously [22,25,26]. Pd and Pd–Pt catalyst amounts in the lean combustion corresponded to 1.2 mg Pd loading in the reactor, and 1.2 mg Pt loading for the monometallic Pt catalyst. The methane-lean feed consisted of a gas mixture of 10 vol.% CH₄ in N₂ (8.5 ml/min standard temperature and pressure STP) and dry or wet (5 vol.% water) air (205 ml/min STP), for a CH₄ concentration of approximately 4000 ppm in the feed. The reactor temperature was increased stepwise from 200 to 550 °C at a rate of 3 °C/min and kept at each temperature for 30 min to investigate

the catalytic performance in a heating ramp (ignition test). These conditions correspond to the data points measured during the in situ XAS. When indicated, the catalysts were reduced in situ prior to the reactions at 350 °C for 2 h in hydrogen.

The ignition tests in the dry methane-rich feed were conducted at a methane-to-oxygen stoichiometric ratio of 1:1, which is below the stoichiometric 1:2 ratio. Pd and Pd–Pt catalyst amounts corresponded to 0.6 mg Pd loading in the reactor and 0.6 mg Pt loading for the monometallic Pt catalyst. The methane-rich feed consisted of a gas mixture of 10 vol.% CH₄ in N₂ (8.5 ml/min STP) and 2 vol.% O₂ in N₂ (42.5 ml/min STP). All the gas mixtures (Praxair) were certified.

3. Results

3.1. Catalytic performance in the lean feed

Fig. 1 shows the ignition curves obtained with Pd, Pt, and Pd–Pt catalysts in the feed with and without an added 5 vol.% water. Catalyst amounts corresponded to 1.2 mg of Pd in the Pd and Pd–Pt catalysts and 1.2 mg of Pt in the Pt-only catalyst. In the dry feed, reduced monometallic Pd and Pd–Pt catalysts (350 °C for 2 h in H₂) were found to show behavior identical to the calcined-only samples with 3% deviation in methane conversion. Palladium is known for its higher activity in lean methane combustion compared with that of platinum [27–29]. In the dry feed, the Pd–Pt bimetallic catalyst exhibited lower activity than monometallic Pd, which was attributed to the increased fraction of inactive Pd (0) vs. active PdO in the presence of Pt [22]. However, Pt-containing catalysts were not significantly affected by the water addition to the stream, whereas Pd was poisoned (Fig. 1), which is line with earlier findings by other groups on the beneficial effect of the addition of Pt to Pd for wet combustion [2,3,19–21]. Reduced Pd catalyst, when exposed to the wet feed, exhibited even lower conversion than its calcined form.

CO chemisorption performed on the catalysts before and after the catalytic tests showed that the Pd catalyst maintained its 1.7 nm Pd particle size, whereas Pt sintered from 5.7 to 9.1 nm particles. The bimetallic catalyst showed a relatively insignificant particle increase from 2.5 to 2.7 nm (Table 1). Platinum is known for its low thermal stability, which can be improved by the addition of palladium [30,31]. Thus, the observed drop in activity for Pd catalyst cannot be explained by a potential loss in active surface area.

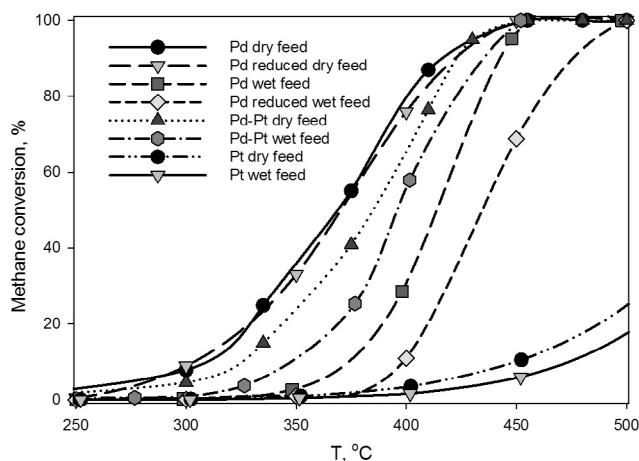


Fig. 1. Ignition curves in dry and wet lean methane combustion. Catalyst amounts correspond to 1.2 mg Pd in Pd-containing catalysts and 1.2 mg in the Pt-only catalyst. The catalysts were calcined prior to the reactions, unless otherwise stated.

Download English Version:

<https://daneshyari.com/en/article/6455477>

Download Persian Version:

<https://daneshyari.com/article/6455477>

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