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Methane oxidation over alumina supported platinum investigated by time-resolved *in situ* XANES spectroscopy

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Abstract

In situ time-resolved X-ray absorption spectroscopy and mass spectrometry were used to correlate changes in catalyst surface composition with catalytic activity for methane oxidation over alumina supported Pt. Different transient experiments (i.e., pulsing of oxygen or hydrogen to an otherwise constant gas composition) were performed to study the methane oxidation kinetics. Changes in the surface O/Pt ratio were monitored by the introduction of a new analysis method of the white line area corresponding to the Pt L_{III}-edge XANES spectra. The relevance of the method was confirmed by first-principles calculations demonstrating how hydrogen and oxygen adsorbates modify the electronic structure of Pt. The experimental results show that during the gas-phase transients, the surface O/Pt ratio changes, which in turn affects the methane oxidation rate. Activity maxima are observed for an intermediate surface O/Pt ratio. An oxygen-rich surface seems to hinder the dissociative adsorption of methane, leading to low methane oxidation activity at oxygen excess.

Keywords: Heterogeneous catalysis; Transient methods; X-ray absorption spectroscopy; Dissociative adsorption; Platinum oxide; CH_4; Pt; Pt/Al_2O_3

1. Introduction

The growing concern about global warming has stimulated strategies to reduce anthropogenic emissions of greenhouse gasses like carbon dioxide (CO_2). One such initiative within the transportation sector is to replace vehicles with gasoline or diesel engines with natural gas vehicles (NGVs). Since natural gas essentially is methane (CH_4), NGVs may reduce CO_2 emissions if the used methane is produced from regenerable sources, e.g., biomass. Moreover, NGVs have other advantages, such as low particulate and NO_x emissions as compared with, for example, standard diesel vehicles. But because CH_4 is also a significant greenhouse gas [1], the methane slip from the combustion process must be controlled, preferably by efficient catalytic exhaust aftertreatment systems. The rather cold exhaust ($<500\,^\circ C$) from these engines demands low-temperature active catalysts.

The most common catalysts for methane oxidation are Pd and Pt. Palladium is more active in the oxidised state and consequently is preferred for operation at net-oxidizing (lean) conditions, whereas Pt, which is more active in the metallic state, may be beneficial for net-reducing (rich) conditions [2–4]. Among the hydrocarbons, methane is the most difficult to oxidize, as reflected by the relatively high temperatures required for the catalytic oxidation to proceed. From a mechanistic standpoint, the low reactivity of methane is connected to the difficulty in which adsorption occurs on different catalytic surfaces. For example, the sticking probability of methane on noble metals is relatively low compared with that on higher alkanes [5]. This indicates that properties like the chemical state and morphology of the surfaces, which are crucial for the adsorption, are important for the overall oxidation rate. For example, it has been shown that the methane conversion over a Pt/Al_2O_3 catalyst strongly depends on the oxidizing–reducing character of the exhausts, in which excess oxygen conditions result in low

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activity [6]. The latter was assumed to be due to deactivation of the Pt crystallites by adsorbed oxygen, decreasing the ability of the catalyst surface to dissociate methane.

X-ray absorption spectroscopy (XAS) is a powerful technique for analysis of, for example, the oxidation state of solids, and thus is used in many fields of research, including chemical sensors, semiconductors, and catalysts [7]. In an XAS spectrum, the extended X-ray absorption fine structure (EXAFS) region provides information on the local geometry and neighboring atoms of the absorbing atom [8]. The EXAFS spectra are sensitive to thermal vibrations and may degrade significantly at temperatures above 300 °C [9], that is, slightly below typical reaction temperatures for oxidation of saturated hydrocarbons over noble metals. But at these temperatures, it is still possible to deduce valuable information from XAS by using the region close to the absorption edge, the so called X-ray absorption near-edge structure (XANES) region. The XANES spectra provide information about the electronic structure of the absorbing atom and thus can reveal information about the chemical state of catalyst surfaces. For example, XANES has been used to study hydrogen [10–12] and CO chemisorption [12], as well as the influence of support material on the chemical state of Pt for typical supported catalysts [13]. The intensity of the absorption edge, the so-called white line [14], is connected to electron transitions from the atomic $2p_{3/2}$ state to the $5d_{3/2}$ and $5d_{5/2}$ levels. An intense white line is observed if the absorbing atom has a large number of d-electron vacancies. Consequently, the white line can be correlated to the oxidation state of platinum as the electron vacancies in the 5d levels reflect the oxidation state of the metal. For oxidized platinum, an intense white line is observed, as opposed to metallic platinum, where the white line is significantly less intense. Different methods based on the height and/or area of the white line have been used to extract quantitative information from XANES measurements [15]. Somewhat more sophisticated methods involving mathematical analysis of the area under the white line by fitting an arc tangent and a Gaussian or Lorentzian function to the spectra also have been used [16,17]. We previously reported the use of the energy difference at the inflection point of the absorption edge as a basis for analysis [18].

In the present study, we introduce a new method that uses the Pt L_{III} white line area (WLA) intensity to facilitate efficient evaluation of time-resolved *in situ* XANES measurements of methane oxidation over a Pt/Al_2O_3 catalyst at transient inlet conditions. Specifically, we correlate changes in the surface O/Pt ratio to methane oxidation activity during oxygen or hydrogen pulsing. To support the interpretation of the results that the method yields, we perform a set of first-principles calculations to study changes of the metal electronic density of states on O and H chemisorption.

2. Experimental

2.1. Catalyst preparation and characterization

A 4% Pt/Al_2O_3 catalyst was prepared by wet impregnation. The support material, 3.8 g γ-Al_2O_3 (SCC a-150/200, Sasol), was dispersed in 10 g of distilled water, and the pH was adjusted to 2.5 by adding diluted HNO_3 solution (Merck). An aqueous platinum nitrate solution ($Pt(NO_3)_2$, 0.15 wt%, Johnson Matthey) was added dropwise to the alumina slurry under continuous stirring to yield a Pt loading of 4%. The slurry was kept under continuous stirring for 20 min, frozen with liquid nitrogen, and freeze dried. To preserve a high Pt dispersion, the catalyst was calcined at 450 °C for 4 h in air, starting with a temperature ramp from room temperature at a rate of 5 °C per minute to 450 °C. The platinum dispersion of the final catalyst was determined by CO chemisorption (Micromeritics, ASAP2010C) at 27 °C, giving 65% dispersion assuming a maximum CO/Pt ratio of 0.8, which is reasonable for highly dispersed Pt particles [19]. The BET surface area (Micromeritics Tristar) of the sample was measured as 182 m^2/g.

2.2. In situ *XANES measurements*

Energy-dispersive *in situ* XANES measurements at the Pt L_{III}-edge (11.6 keV) were performed in transmission mode at beamline ID24 at ESRF, Grenoble, France, on a pressed pellet ($\varnothing = 5.3$ mm and $l = 1.3$ mm) of ca 50 mg 4% Pt/Al_2O_3 and 50 mg KBr. The x-ray beam spot size on the sample was $\sim 200 \times 200$ µm, and the data sampling rate was 0.56 s. The pellets were mounted in a temperature-controlled flow reactor cell, to which a reactant gas mixture, obtained through individual mass flow controllers, was introduced. A total flow of 100 ml/(NTP)min, corresponding to a space velocity of about 70,000 h^{-1}, was used. The reactor cell was mainly a flow-by type with a volume of ~ 5 ml, here resulting in a residence time of <3 s. The product stream was continuously analyzed with a Balzers Prisma mass spectrometer following the H_2 (m/e 2), He (m/e 4), CH_3 (m/e 15), H_2O (m/e 18), CO (m/e 28), O_2 (m/e 32), Ar (m/e 40), and CO_2 (m/e 44) signals. The beamline was equipped with a Si [111] polychromator crystal, operating in Bragg mode, for selection of the desired range of X-ray wavelengths (11.43–12.05 keV), and a 1152 × 1242 pixel CCD solid-state detector for spectral analysis. Two additional mirrors in the beamline were used to achieve harmonic rejection. The estimated energy resolution was $\Delta E/E \approx 1.2\text{–}1.5 \times 10^{-4}$, and the energy increment between data points was 1.2 eV. The XANES spectra were recorded during pulse response (PR) experiments while the oxidising-reducing character of the feed was periodically varied by changing either the oxygen concentration between 0 (5 min) and 1250 vol-ppm (5 min) using a 500 vol-ppm CH_4 flow or a H_2 concentration between 0 (5 min) and 5000 vol-ppm (5 min) using a flow of 500 vol-ppm CH_4 and 1250 vol-ppm O_2. Helium was used as carrier gas in all experiments. The PR experiments were repeated at 450, 400, and 350 °C. All of the experiments are summarized in Table 1 together with the stoichiometric number, S, which is used to describe the oxidizing–reducing characteristics of the feed gas.

2.3. Method for evaluation of XANES spectra

Previously, the WLA was evaluated by fitting an arc tangent and Gaussian or Lorentzian function to the peak and then