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Experimental data and kinetic modeling of the catalytic and electrochemically promoted CH_4 oxidation over Pd catalyst-electrodes

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HIGHLIGHTS

- The kinetic of the electrochemically promoted methane oxidation over Pd based catalyst-electrodes is studied.
- A model based on Langmuir–Hinshelwood mechanism predicts the kinetic.
- The model predicts the data under both open circuit state and polarization conditions.
- CH_4 adsorption equilibrium constant increases with increasing applied anodic potential.

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ABSTRACT

This aim of this work is to model the kinetics of the electrochemically promoted methane oxidation over impregnated Pd catalyst-electrodes in the temperature range between 300 and 400 °C. Six different kinetic models based on the Eley–Rideal, Langmuir–Hinshelwood and Mars van Krevelen mechanisms were fitted to the experimental data. It was found that Langmuir–Hinshelwood mechanism, considering dissociative chemisorption of O_2 and only one oxygen surface species consumed in the rate determining step, successfully predicted the kinetics of the methane consumption rate under both open circuit state and electrochemical promotion conditions. In addition, the influence of the polarizations on the components adsorptions was analyzed. An increase in the adsorption constant and the partial charge transfer parameter of the methane was obtained with increasing values of the applied anodic potential.

1. Introduction

Catalytic combustion of methane is of actual interest as a mean for generating power with minimal formation of NO_x, and as removing small amounts of methane from emissions coming from methane-burning engines [1,2]. Consequently, catalytic combustion of natural gas is also being explored as a route for the production of heat and energy in view of its capability to achieve effective combustion at much lower temperatures than those reached in conventional flame combustors, hence leading to lower emissions [3,4].

On the other hand, lean burn natural gas vehicles (NGVs) are now commercially available in service vehicles as a viable approach to meet particulate and gaseous emission standards in urban environments. However, methane is the main hydrocarbon species emitted by these vehicles, so the development of efficient catalysts is required to control methane emissions [5,6].

The kinetics and mechanism of the catalytic oxidation of hydrocarbons has been extensively studied in the past. The development of kinetic models able to predict the effect of the temperature and reactants partial pressure on the catalytic activity is required for designing catalytic converters. There is a general agreement that the rate of the methane oxidation over supported palladium is near zero order with respect to the oxygen partial pressure and first order with respect to the methane partial pressure [7–14]. This rate law would justify the initial slow activation step. It has been also found that only one C–H bond is broken in the initial dissociative adsorption of methane leading to the formation of adsorbed hydrogen and methyl radicals. Thus, activation of the first C–H bond has been proposed to be the rate-limiting step of the oxidation process [7,8,15].

Although several studies have been reported in the literature related to the CH_4 oxidation kinetics over Pd catalysts, there is no unanimity about the mechanisms of this reaction. Hence,

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Langmuir–Hinshelwood (LH) [11,16,17], Eley–Rideal (ER) [18,19] and Mars van Krevelen (MvK) [20–22] mechanisms have been proposed. In fact, the nature of the active catalyst has been the subject of some controversy. Palladium owes its unique reactivity to the formation and participation of palladium oxide in the surface. Therefore, some synergism between palladium metal and some form of PdO_x should be considered [8,23–25].

During the last years, the possibility of enhancing the catalytic activity by applying small currents or potentials between a catalyst (acting as the working electrode) supported on a solid electrolyte, and a counter electrode also supported on the same electrolyte, has been investigated. This phenomenon, firstly introduced by the group of Prof. Vayenas in the early 80s [26–29], is called Electrochemical Promotion of Catalysis (EPOC) or Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) and originates from the controlled migration of promoting species from the electrolyte support to the catalytic metal/gas interface during polarization. These backspillover ionic species form an overall neutral double layer at the catalyst-gas interface. This "effective double layer" affects catalytic rates by modifying the catalyst work function, i.e. the binding energy of chemisorbed reactants and intermediates primarily via lateral electrostatic interactions [30]. Thus, it has been shown conclusively that electrochemical promotion is an electrically controlled metal-support interaction and at least certain types of metal-support interactions are induced by reverse spillover of promoter species from the solid electrolyte onto the surface of the catalyst-electrode [31].

The approach of the kinetic models does not take into account the electrostatic interaction between the dipole of the adsorbate and the field of the "effective double layer" [30]. In this sense, Brosda and Vayenas [32,33] appropriately modified the Langmuir isotherm taking into account explicitly the application of the potential, i.e. the attractive or repulsive electrostatic interactions between the adsorbates and the "effective double layer" present at the catalyst-gas interface. Thus, they established the modified electrochemical Langmuir or effective double layer isotherm:

$$\theta_j/(1-\theta_j) = K_j p_j \exp(\lambda_j \Pi) \tag{1}$$

where θ_j, K_j and p_j correspond with the coverage, the adsorption equilibrium constant and the partial pressure of the molecule j, respectively. λ_j is the partial charge transfer parameter, i.e. the net number of electrons donated by the adsorbate S_j to the metal during the chemisorptive bond formation. Thus, λ_j is zero for a truly covalent chemisorptive bond, positive for an electron donor adsorbate and negative for an electron acceptor adsorbate. The partial electron transfer parameter λ_j is directly related to the dipole moment of adsorbed molecule j [33]. And Π is the dimensionless potential defined by the next equation [30]:

$$\Pi = U_{WR}F/RT \tag{2}$$

where U_{WR} is the catalyst potential, F is the Faraday's constant, R is the gas constant and T is the temperature.

In this work, a discrimination study among different models that takes explicitly into account the electrostatic interactions between catalytic adsorbates, the effective double layer present at the catalyst–gas interface and the catalytic oxidation of methane under both open circuit and electrochemical promotion conditions was carried out.

2. Experimental

A Pd/YSZ/Au electrochemical cell was used in this study. YSZ pellet (8 mol % Y_2O_3-stabilized ZrO_2, YSZ), of 19 mm diameter and 1 mm thickness (Henson Ceramics Limited) was used as the solid electrolyte. Inert gold counter and reference electrodes were deposited on one side of the solid electrolyte pellet by application of thin coatings of gold organometallic paste (Gwent Electronic Materials C1991025D2) followed by calcination at 850 °C for 2 h. A porous palladium catalytic film serving as the working electrode was deposited on the other side of the YSZ by using impregnation technique as described in more detail elsewhere [34,35]. This way, palladium catalyst-working electrode was prepared by successive steps of deposition and thermal decomposition of a palladium precursor solution. An aqueous solution of 0.1 M $[Pd(NH_3)_4](NO_3)_2$ (Sigma–Aldrich) was used as the precursor. The evaporation of the solvent took place at 100 °C for 10 min, followed by drying of the sample at 120 °C overnight and then calcination at 450 °C for 2 h with a 5 $°C\,min^{-1}$ temperature ramp. The geometric surface area of the catalyst-electrode was 2 cm^2 and the final Pd loading was 0.85 mg Pd.

The experiments were carried out in a single chamber quartz reactor, as described elsewhere [30]. Reactants were certified standards of CH_4 and O_2. They were further diluted in pure He to adjust the total gas flow rate at 200 $cm^3\,min^{-1}$ (STP). Prior to the experiments, the catalyst was pre-treated for stabilization under 20 kPa O_2 (100 $cm^3\,min^{-1}$, STP) at 300 °C for 2 h, following to a thermal cycle from 150 to 450 °C and then cooling by passing the next gas mixture: 0.3 kPa C_2H_4, 4.5 kPa O_2 (200 $cm^3\,min^{-1}$, STP [35]) Gas analysis of the reactants and products was performed using an on-line gas-microchromatograph (Varian CP-4900). Constant potentials or currents were measured and imposed by using a potentiostat–galvanostat Voltalab PGZ 301 (Radiometer Analytical).

The present kinetic study was based on the data of methane consumption rate ($-r_{CH4}$). Different possible rate equations based on Eley–Rideal, Langmuir–Hinshelwood and Mars van Krevelen mechanisms were fitted to the experimental data. For that purpose, a VBA-Excel application was developed to solve the proposed kinetic models [36–39]. The Bader-Deufhard method was used in the evaluation of the set of ordinary differential equations [40], whereas the Marquardt–Levenberg algorithm was used in the nonlinear regression procedure [41,42]. The weighted sum of the squared differences between the observed (Exp) and calculated (Th) reaction rate was minimized according to the following equation [38]:

$$SSQ = \sum_{i=1}^{n}\left[(-r_{CH_4})_{iExp} - (-r_{CH_4})_{iTh}\right]^2 \tag{3}$$

The discrimination of the kinetic models was performing according to the statistical F-test, which has an F-distribution under the null hypothesis. The procedure was based on the tabulated value of F (F-test) and F_c defined by the following equation [41,43]:

$$F_c = \frac{\sum_{i=1}^{n}\left[(-r_{CH_4})^2_{iTh}/p\right]}{\sum_{i=1}^{n}\left[(-r_{CH_4})^2_{iExp} - (-r_{CH_4})^2_{iTh}\right]\Big/(n-p)} \tag{4}$$

where n represents the number of experiments and p the total number of parameters.

If F_c is larger than $F(p, n-p, 1-\alpha)$, assuming a value of $\alpha = 0.05$ (95% confidence level), the regression was considered to be meaningful, although there is no guarantee that the model is statistically suitable since meaningfulness of each parameter in the model must be also evaluated. Hence, a complementary test, named t-test, was used. The t-test considers that the statistical hypothesis test follows a Student's t distribution and allows for verifying if the estimation of the parameter b_{fi} differs from a reference value (generally zero). Thus, a parameter is meaningful if the following inequality occurs:

$$t_{ci} = t(n-p, 1-\alpha/2) \tag{5}$$