

# Determination of Kinetic Parameters for Methane Oxidation over Pt/γ-Al<sub>2</sub>O<sub>3</sub> in a Fixed-Bed Reactor

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**Abstract.** This paper describes a kinetic study for the determination of the kinetic parameters of lean methane emission oxidation over  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub> in a dedicated laboratory scale fixed bed reactor. A model of the mechanistic reaction kinetic parameters has been developed. The reaction rate model was determined using the rate-limiting step method, which was integrated and optimized to find the most suitable model and parameters. Based on this study, the Langmuir-Hinshelwood reaction rate model with the best correlation is the one where the rate-limiting step is the surface reaction between methane and one adsorbed oxygen atom. The pre-exponential factor and activation energy were 9.19 × 10<sup>5</sup> and 92.04 kJ/mol, while the methane and oxygen adsorption entropy and enthalpy were -17.46 J/mol.K, -2739.36 J/mol,-16.34 J/mol.K, and -6157.09 J/mol, respectively.

**Keywords:** catalytic oxidation; fixed bed reactor; kinetic parameter; Langmuir-Hinshelwood; methane; oxidation;  $Pt/Al_2O_3$ .

### **1** Introduction

Fugitive methane emissions from coalmines around the world represent approximately 8% of the world's anthropogenic methane emissions, which constitutes a 17% contribution to the total anthropogenic greenhouse gas emission [1]. There are several technical ways to abate the methane concentration in the air, such as oxidation of methane to carbon dioxide. This method is widely preferred because methane oxidation offers some extra benefits. In addition to reducing the global warming potential, it also generates heat, which can be used as a source of energy if it could be captured. Although this reaction produces carbon dioxide, this method can reduce the greenhouse effect up to 87% [2].

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Methane emission due to leakage from natural gas piping systems and coalmines occurs in low concentrations, typically around 0.1-1 volume %, and its value changes over time, depending on the air flow rate. This value is beyond the flammability limit of methane (5-16 volume %). To avoid the use of flames for oxidizing the methane, catalytic oxidation offers benefits to abate the methane. The most commonly used catalysts for methane oxidation are noble-metal-based catalysts, such as Pd and Pt [3]. Pd catalyst is more active compared to Pt catalyst, but Pt catalyst is more resistant to sulfur poisoning. Therefore, Pt catalyst is preferred for this application [4].

The concentration changes of methane as aforementioned can result in a different reaction rate and reactor performance. Dynamic operation can increase the average conversion of methane compared to steady state conversion [5]. According to Carlsson, *et al.* [6], the differences in the reaction conversion are caused by differences in the catalyst state. Dynamic operation can drive the catalyst to achieve its optimum condition, which cannot be achieved with steadystate operation. For  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the optimum condition occurs when the active site is neither completely reduced nor fully oxidized [7]. This state induces the reaction kinetic parameters determined through a power law model become hard to apply to systems in dynamic conditions. In a power law model, the adsorption-desorption steps don't have to be included, whereas in a mechanistic model they do. Development of the mechanistic reaction kinetic parameters is required to overcome this obstacle.

According to Hurtado, *et al.* [8], methane oxidation over Pd-based catalyst follows the Mars van Krevelen reaction mechanism, which means the reaction occurs due to alternating oxidation and reduction over the catalyst surface. This may be possible when the Pd catalyst state is completely oxidized. On the other hand, Pt catalyst becomes less active when it is completely oxidized [9]. Cortes, *et al.* [10] stated that the Mars van Krevelen and Langmuir-Hinshelwood reaction mechanisms for methane oxidation over Pt catalyst are indistinguishable. Therefore, the kinetic parameters according to the Langmuir-Hinshelwood reaction mechanism werechosen asthe reaction mechanism.

The objective of this study was to develop an appropriate kinetic model and its parameters according to the Langmuir-Hinshelwood reaction mechanism for methane oxidation over a commercial 3%  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in a fixed-bed reactor. The outcome of this investigation consists of the kinetic data for a reactor design that is dedicated to transient operation.

## 2 Experiment

### 2.1 Materials

A commercial Pt catalyst on gamma alumina with an active metal content of 3% (w/w) was used in this study. The catalyst was in spherical form with a diameter of two mm. Some of the catalyst was crushed for the internal mass transfer testing. The reactants used were methane and air. Alumina was also used inside the reactor as inert material to approach a plug flow reactor character. Silica gel was used to adsorb water in the inlet and outlet gas stream.

## 2.2 Experimental Setup

The methane and air used for the experiment flowed from pressurized gas cylinders. Each gas stream was connected to a bubble soap meter measuring the volumetric flow rate of each gas. A tubular fixed-bed reactor with a diameter of 10 mm was used. The catalyst bed and inert bed length were 10 mm and 50 mm, respectively. The reactor was equipped with a furnace and a controller in order to ensure that the reactor temperature was constant (isothermal). A thermocouple was used to measure the catalyst-bed temperature. Silica gel was added in the reactant and product flow to adsorb any water content. The reactants and products were analyzed by Gas Chromatograph (GC) GC-8A and Chromatopac CR 1-Busing argon as gas carrier. Figure 1 shows the experimental setup of the fixed-bed reactor for methane oxidation.

## 2.3 Experimental Procedure

Air with a volumetric velocity between 1 ml/s until 12 ml/s was flowed from the pressurized gas cylinders while heating of the reactor was conducted. When the reactor reached a certain temperature, methane was flowed into the reactor so 5% (v/v) methane in air mixture was formed as the reactant. The reactant and products were periodically analyzed using an offline GC. The methane conversion can be defined as:

$$Methaneconversion(\%) = \frac{\left(\frac{methanearea}{nitrogenarea}\right)_{input} - \left(\frac{methanearea}{nitrogenarea}\right)_{output}}{\left(\frac{methanearea}{nitrogenarea}\right)_{input}} \quad (1)$$

Oxygen conversion can be calculated using a similar equation. All experiments were performed under steady state conditions.



Figure 1 Experimental apparatus.



Figure 2 SEM figure of catalyst surface.



Figure 3 X-ray diffractogram.

## 2.4 Catalyst Characterization

The BET specific surface area of  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub> was determined using a NOVA surface area analyzer. It was found that the catalyst surface area was 196 m<sup>2</sup>/gram. Scanning electron microscopy was used to study the surface morphology. The SEM figure of the catalyst is shown in Figure 2. The SEM figure confirms that the catalyst surface was porous. XRD testing showed that the catalyst consisted of platinum and alumina (Al<sub>2</sub>O<sub>3</sub>). The X-ray diffractogram is shown in Figure 3.

## 3 Results and Discussion

### 3.1 Line-Out Procedure

A line-out procedure was carried out as a preliminary test to determine the time when the catalyst reached a constant state of activity. Constant state of activity was shown by steady conversion. According to Campman [11], the catalyst has a higher activity during the start-up period as compared to the period after the reaction takes place. The experimental results for the line-out procedure are shown in Figure 4.

The conversion of methane exhibited complete reaction at the beginning of the process, just after the methane and oxygen were fed to the reactor. For the subsequent sampling, the conversion of methane decreased to 49% at t = 180 min, 45% at t = 205 min, and 50% at t = 235 min. This confirmed the statement

of Campman [11] that catalyst activity is very high at the beginning. For oxygen, the conversion was 21% during the initial period, then increased to 30%, and eventually decreased to 21%.



Figure 4 Line-out procedure profile.

At t = 0 min, methane was introduced into the catalytic fixed-bed reactor. The first sample was taken at t = 15 min, but methane was not detected in the system. Methane could be detected from t = 43 min. Methane conversion at this point was 100%, but the oxygen conversion was 22%, *i.e.* lower than its stoichiometric conversion. This shows that the feed mixture had not reached the right composition. When the next sample was taken, at t = 75 min, the oxygen conversion obtained in the experiment had reached its stoichiometric conversion, showing that the reactant composition had already reached the intended value.

The catalyst activity reached a constant value at t = 180 min. This can be seen from the methane conversion at t = 180 min, which was similar to the conversion at t = 235 min. The oxygen conversion obtained at this time (21%) approached the stoichiometric conversion of oxygen. Based on this line-out procedure, the main experiment should be carried out 180 min after the methane was flowed to the system.

### 3.2 Mass Transfer Testing

External mass transfer testing was carried out solely through the laboratory experiment in the fixed-bed reactor. The experiment was conducted by changing the volumetric flow rate in the reactor while keeping the time space constant at an operating condition of 540  $^{\circ}\rm C$  and a spacetime of 185 gram. hour/mole of methane. The experimental result is presented in Figure 5.



Figure 5 Methane conversion to volumetric flow rate profile.

In the first condition, when the volumetric flow rate was set to 0.03 ml/s, 0.04 ml/s, and 0.05 ml/s, the methane conversions were 72%, 49%, and 50%, respectively. In the second condition, the methane conversion values for all variations were almost the same, between 21% and 23%.

The conversion for the 0.03 ml/s volumetric flow rate was higher than the methane conversion for the other volumetric flow rates. This shows that the external mass transfer effect was apparent in the first volumetric flow rate variation. When the volumetric flow rate increased to 0.05 ml/s and 0.06 ml/s, both of these variations resulted in the same methane conversion. In these higher volumetric flow rates, the external mass transfer effect was so small that it could be ignored.

Internal mass transfer testing was carried out by changing the catalyst diameter. There were three variations used in this test: powder catalyst with a diameter between 0.345 and 0.599 mm (variation 1); powder catalyst with a diameter between 0.599 and 0.710 mm (variation 2); and spherical catalyst with a 2 mm diameter (variation 3). All variations were performed at the same operating conditions: 540 °C and a spacetime of 185 gram.hours/mole of methane. The experimental resultis shown in Figure 6.

The methane conversion values obtained in variations 1, 2 and 3 were 51%, 50%, and 50%, respectively. All three variations resulted in the same methane conversions. It can be concluded that the internal mass transfer effect in all

variations was small and could be ignored. Therefore, any diameter variation tested could be used. In this experiment, the spherical catalyst was used.



Figure 6 Methane conversion to catalyst diameter profile.

### 3.3 Kinetics Studies

After conducting the preliminary experiments, the main experiment could be conducted. The minimum volumetric flow rate used was 0.05 ml/s. The amount of catalyst used in the main experiment was kept constant at 0.5 grams. The temperature variations used were 500 °C, 520 °C, 540°C. Figure 7 and 8 show the conversion to temperature profile for various spacetimes for methane and oxygen.



**Figure 7** Methane conversion-to-temperature profile at various spacetimes. Spacetimes in gram.hour/mole of methane.



Figure 8 Oxygen conversion-to-temperature profile at various spacetimes. Spacetimes in gram.hour/mole of methane.

Both of the profiles in Figures 7 and 8 show the same tendency. Increasing the reaction temperature caused an increase of methane and oxygen. When the spacetime increased, methane and oxygen conversion also increased.

Four models of the Langmuir-Hinshelwood reaction rate were derived by assuming the rate-determining step. Each model contained the reaction rate constants (k) and equilibrium adsorption constants (K).

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

$$K = \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \tag{2}$$

All the models were integrated, while the parameters were guessed and optimized. The objective function used in optimization was defined as follows:

$$FOBJ = \left(\frac{C_{data} - C_{model}}{C_{data}}\right)^2 \tag{3}$$

The reaction rate models with their respective rate parameters are shown in Table 1. Figures 9 until 11 show the comparison graph between the experimental and simulation data for each model.

Model	Rate determining step	Rate expressions	Rate parameters	R <sup>2</sup>
LH1	Methane adsorption	$r = \frac{k_1 C_{CH4}}{1 + \sqrt{K_2 C_{02}}}$	$k_1 = 1488.72 \times \exp\left(\frac{-82245.41}{RT}\right)$ $K_2 = \exp\left(-\frac{8373.61}{R} + \frac{44640.9}{RT}\right)$	0.846
LH2	Oxygen adsorption	$r = \frac{k_2 C_{02}}{(1 + K_1 C_{CH4})^2}$	$k_{2} = 1.26 \times \exp\left(\frac{-48201.58}{RT}\right)$ $K_{1} = \exp\left(-\frac{231.94}{R} + \frac{3048.74}{RT}\right)$	0.745
LH3	Surface reaction between adsorbed methane and one atomic adsorbed oxygen	$r = \frac{k_3 K_1 C_{CH4} \sqrt{K_2 C_0}}{\left(1 + K_1 C_{CH4} + \sqrt{K_2 C_0}\right)}$	$k_{3} = 919419.05 \times \exp\left(\frac{-92042.71}{RT}\right)$ $K_{1} = \exp\left(-\frac{17.46}{R} + \frac{2739.36}{RT}\right)$ $K_{2} = \exp\left(-\frac{16.34}{R} + \frac{6157.09}{RT}\right)$	0.851
LH4	Surface reaction between adsorbed methane and two atomic adsorbed oxygen	$r = \frac{k_3 K_2 K_1 C_{CH4} C_{O2}}{\left(1 + K_1 C_{CH4} + \sqrt{K_2 C_2}\right)}$	$\overline{\overline{c_{02}}}^3$ Parameters not obtained	-
, E	8.E-04		= <sup>4.E-03</sup>	
ncentratio	6.E-04 5.E-04		3.E-03	
[ethane Co	4.E-04 3.E-04 2.E-04		2.E-03	
E E	0 50	100 150 200 Space time	0 50 100 150 20 Space time	0

 Table 1
 Methane oxidation kinetic parameters.

**Figure 9** Experimental data (symbols) and simulation data (lines) for methane and oxygen concentration at various spacetimes and temperatures for model LH1. The diamond-solid lines represent data at 500°C; the square-dotted lines represent data at 520°C; the triangle-dashed lines represent data at 540°C. Spacetime in gram.hour/mole of methane.



**Figure 10** Experimental data (symbols) and simulation data (lines) for methane and oxygen concentration at various spacetime and temperature for model LH2. The diamond-solid lines represent data at 500°C, the square-dotted lines represent data at 520°C, the triangle-dashed lines represent data at 540°C. Spacetime in gram.hour/mole of methane.



**Figure 11** Experimental data (symbols) and simulation data (lines) for methane and oxygen concentration at various spacetime and temperature for model LH3. The diamond-solid lines represent data at  $500^{\circ}$ C, the square-dotted lines represent data at  $520^{\circ}$ C, the triangle-dashed lines represent data at  $540^{\circ}$ C.

Model LH1 was derived using methane adsorption as the rate-limiting step. Model LH2 assumed dissociative oxygen adsorption as the rate-limiting step. Both model LH3 and LH4 were derived by assuming surface reaction between adsorbed methane and adsorbed oxygen as the rate-limiting step. The difference between model LH3 and LH4 was the number of adsorbed oxygen atoms involved in the reaction. In model LH3, only one adsorbed oxygen atom was involved in the surface reaction, while model LH4 assumed two adsorbed oxygen atoms were involved in the surface reaction. All the parameters in Table 1 satisfied the basic thermodynamic requirement that the values of the pre-exponential factor and the activation energy have to be positive, while the adsorption entropy and enthalpy change has to be negative. The parameters for model LH4 are not shown because they did not fulfill this requirement.

As can be seen in Table 1, the best correlation was achieved with model LH3. Therefore it can be assumed that the methane oxidation reaction followed the Langmuir-Hinselwood reaction mechanism with a surface reaction between the adsorbed methane and one adsorbed oxygen atom as the rate-limiting step. The LH3 model also satisfied the additional thermodynamic requirement that the natural value of a species' adsorption entropy change cannot exceed its entropy in the gas phase. The gas entropy for methane and oxygen was 186 J/mole.K and 205 J/mole.K, respectively, while the adsorption entropy change for methane and oxygen was -17.46 J/mole.K and -16.34 J/mole.K, respectively. Therefore, the parameters in model LH3 fulfilled the additional thermodynamic requirement.

The reaction mechanism obtained from this study corresponded to several experiments that have been conducted by researchers such as Hurtado, *et al.* [8] and Pengpanich, *et al.* [12]. Although the catalyst used by Hurtado, *et al.* and Pengpanich, *et al.* was different from the catalysts used in this study, both experiments showed that the methane oxidation reaction followed the Langmuir-Hinshelwood reaction mechanism, which assumes that the rate determining step is surface reaction between the adsorbed methane and one adsorbed oxygen atom. This reaction rate model also showed that oxygen adsorption was faster than methane adsorption, resulting in chemisorption of methane onto the catalyst surface [12].

### 4 Conclusion

Determination of the kinetic parameters following the Langmuir-Hinshelwood reaction rate model has been carried out. It was concluded that the best correlation among the tested models was the reaction rate model that assumes the rate-limiting step is the surface reaction between the adsorbed methane and one adsorbed oxygen atom. The pre-exponential factor and activation energy were  $9.19 \times 10^5$  and 92.04 kJ/mole, respectively, while the methane and oxygen adsorption entropy and enthalpy change were -17.46 J/mole.K, -2739.36 J/mole, -16.34 J/mole.K, and -6157.09 J/mole, respectively.

### Nomenclature

A = pre-exponential factor

- $E_a$  = activation energy
- $F_{ao}$  = initial methane molar flow rate
- H = Enthalpy
- k = reaction rate constant
- K = equilibrium adsorption constant
- R = gas constant
- S = Entropy
- T = Temperature
- W = catalyst weight
- $\Delta$  = Changes
- $\gamma$  = Gamma

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