

Research Article

Oxidation Kinetics of Propane-Air Mixture over NiCo₂O₄ Catalyst Emitted from LPG Vehicles

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Abstract

This paper describes the kinetics of catalytic air oxidation of propane. The kinetics data were collected in a plug flow tubular reactor. The experiments were performed over the NiCo₂O₄ catalyst prepared by co-precipitation method followed by calcination at 400 °C. The kinetic data were collected under the following conditions: 200 mg of catalyst, 2.5 % of propane in air, total flow rate of 60 mL/min, and temperature ranges of 130-170 °C. The data were fitted to the power law rate equation. The activation energy and frequency factor were found to be 59.3 kJ/g mol and 2.9×10^8 (mol)^{0.47}.L^{0.53}/g cat.h, respectively. Copyright © 2017 BCREC Group. All rights reserved.

Keywords: Complete combustion; Oxidation kinetics; HC emissions; propane-air mixture; NiCo₂O₄ catalyst

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1. Introduction

LPG has been used as an alternative fuel for vehicles as early as 1912 but only on a limited scale. It became more popular due to increased demand of cleaner fuel and energy crises in the 1970's and in the 1990's. India recently launched a gasoline/LPG bi-fuel automotive engine into the market [1]. LPG driven vehicles was preferred over conventional fuelled vehicles due to several advantages such as HCs emitted are of short carbon chains with low ozone-forming reactivity; low emission of toxic air contaminants such as benzene and 1,3-butadiene; unlike diesel engines, there are practically no PM emissions from LPG engines; cold-start emissions are low; emissions do not increase drastically with engine wear and deposit

buildup; zero evaporative and running losses due to the sealed fuel system [2]. In addition, the pollutants in exhaust of LPG vehicle is reduced as compare to gasoline vehicle as follows: CO by 30 % in an urban cycle and by 10 % in an extra-urban cycle, HC by 30 % in an urban cycle and by 51 % in an extra-urban cycle, NO_x by 41 % in an urban cycle and by 77 % in an extra-urban cycle, CO₂ by 10 % in an urban cycle and by 11 % in an extra-urban cycle [3]. LPG vehicle should be more reliable than gasoline due to its better specific fuel consumption and improved mileage. Therefore, the Indian government has been inspiring LPG use to reduce ambient pollutant levels in the urban environment.

In spite of all advantages, there are some limitations with LPG vehicles that its exhaust emission still contain high concentrations of light HCs along with other pollutants, such as CO and NO_x [4]. These pollutants have an adverse impact on human health as well as envi-

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ronment also. So, the government has imposed environmental legislation increasingly stringent targets for permissible levels of LPG/petrol automobile emissions, with a target to lessen the emissions. Therefore, abatement of unburned HCs from LPG vehicles is a serious concern. The catalytic oxidation plays a very important role to control these emission of LPG vehicles. The catalytic oxidation is one of the promising techniques to oxidize the HCs into CO₂ and H₂O vapor [5-6]. Since, the LPG contains the major amount of propane (~72 %), therefore propane was selected as a model HC for its oxidation kinetics studies Equation 1.



A better tool of catalyst performance for C₃H₈ oxidation is to report the activation energy for process. The activation energy data are desirable for the modeling and design of the catalytic converter. It is relevant to develop kinetic expressions for catalytic combustion of C₃H₈ also because they can be implemented into CFD models useful for reactor design and optimization [7-8].

In this regard, a few studies have been reported on the kinetic study of catalytic combustion of C₃H₈. The propane combustion over Pt/Al₂O₃ catalyst could be described very well by Langmuir-Hinshelwood model, in which molecularly adsorbed hydrocarbon reacts with dissociatively adsorbed oxygen the reaction order for the fuel lean conditions was found to be 1.1 for propane and 0.6 for oxygen [9] and

0.4 for C₃H₈ and 0.9 for oxygen [10]. Interestingly, for the La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O₃ perovskite oxide catalyst, the best fit for the propane combustion data [11] was obtained with the Mars-van Krevelen kinetic model [12-14], the reaction order was 0.5 and 0.3 with respect to propane and oxygen, respectively [11]. The power law model was also employed for the fitting of oxidation data.

The noble metal has been presented as efficient catalysts than a non-noble metal catalyst for HCs oxidation reaction. Then, in the recent years, considering the high cost, rare availability of noble metal and their instability with impurities, more attention has been focused on transition metal oxide catalyst. In spite of the significant progress in C₃H₈ oxidation studies and the extended literature, there is still uncertainty concerning the corresponding kinetic equations. The reported activation energies of various catalysts are mentioned in Table 1. For comparison, the activation energy determined in the present investigation is also reported in this table. A wide variation in the reported values of activation energies can be visualized in the Table. The basic reason, which leads to the inconsistencies are related to the types of the catalyst and the experimental conditions.

The present work was devoted for the first time to study the kinetics of the air-oxidation of diluted propane over the NiCo₂O₄ catalyst at different temperatures (130-170 °C). Efforts have been made to fit the oxidation data to power law rate equation.

Table 1. Activation energy for catalytic air-oxidation of C₃H₈ reported in the literature

Reference	Catalyst	Temperature (°C)	Activation energy (kJ/mol)
[15]	Mg ₃ AlO	472-600	119.5
	CuMg ₂ AlO	325-435	122.3
	Cu ₂ MgAlO	335-450	125.0
	Cu ₃ AlO	363-475	103.0
	Pd/Al ₂ O ₃	425-600	117.0
[16]	CuO-CeO ₂ /γ-Al ₂ O ₃		62.0
	CuO/γ-Al ₂ O ₃	350-500	95.0
	CeO ₂ /γ-Al ₂ O ₃		102.0
[17]	CuO-CeO ₂ /γ-Al ₂ O ₃	2700-375	74.4
[18]	VMgO	475-550	122±6
[19]	La _{0.66} Sr _{0.34} Ni _{0.3} Co _{0.7} O ₃	200-340	71.0
[20]	Pd/Al ₂ O ₃	280-330	87.7
Present study	NiCo ₂ O ₄	130-170	59.3

2. Materials and Methods

2.1. Catalyst preparation

The NiCo₂O₄ spinel catalyst was prepared by the co-precipitation method described by Klissurski and Uzunova [21]. All chemicals used in preparation of the catalysts were of AR grade. The precursors taken were nitrates of Ni and Co in the molar ratio of 1:2. The solutions of nitrates (2.76 M) were heated to about 75 °C then added rapidly into a solution of Na₂CO₃ (1.4 M and pH 9). The hydroxycarbonate cake was then dried at 110 °C for 24 h and calcined at 300 °C for 3 h.

2.2. Experimental procedure

The catalytic combustion of C₃H₈ over NiCo₂O₄ catalyst was carried out at atmospheric pressure in a fixed bed down flow tubular reactor containing 200 mg of the catalyst was diluted to 5 mL with alumina at different temperatures (140-170 °C) and space velocities (13.82-55.26 g cat./h/gmol). Details of the reactor are given elsewhere [22]. The reactor was placed vertically in a split open furnace. The following reaction conditions were maintained: catalyst particle size 100-150 mesh, using a lean mixture of 2.5 % C₃H₈ (v/v) in air, maintaining the total flow rate at 60 mL.min⁻¹. The flow rate of gases were monitored with the help of digital gas flow meter. The air feed was made free of moisture and CO₂ by passing it through CaO and KOH pellet drying towers. The catalytic experiments were carried out under steady state conditions. Typically, the reactor was heated to the desired temperature with the help of a microprocessor based temperature controller. A temperature control of ±0.5 °C was achieved.

The gaseous reactants and products were analyzed by an online gas chromatograph (Nucon series 5765) equipped with a Porapak Q-column, methanizer and FID detector for the concentration of the propane and CO₂. The fractional conversion of propane (X_P) was calculated on the basis of the values of the concentration of CO₂ in the product stream by the following formula (1):

$$X_P = \frac{\{[C_P]_{in} - [C_P]_{out}\}_i}{[C_P]_{in}} = \frac{\{[A_P]_{in} - [A_P]_{out}\}_i}{[A_P]_{in} = [A_{CO_2}]_f / [A_{CO_2}]_t} \quad (1)$$

where, the change in the concentration of propane due to oxidation at any instant $\{[C_P]_{in} - [C_P]_{out}\}_i$ is proportional to the area of the chromatogram of CO₂ formed at that instant $[A_{CO_2}]_i$, and the concentration of propane in the inlet

stream $[C_P]_{in}$ is proportional to the area of the chromatogram of CO₂ formed $[A_{CO_2}]_t$ at the oxidation of propane. Experiments were performed three times for oxidation of propane and average results were plotted.

3. Results and Discussion

The kinetic parameters for the C₃H₈ oxidation were determined by following the product formation as a function of propane and oxygen under reaction conditions required for a differential operating regime (reactants conversion 50 % at any temperatures used). In these experiments, carbon dioxide is referred as product, since there is no carbon monoxide detected during the reaction at any reaction temperatures. Prior to kinetic study, the catalyst was diluted with inert solid particles of γ -alumina in order to avoid the formation of hot spots in catalytic bed as well as increased heat transfer area of catalyst bed. A blank reaction (γ -alumina only, 5 mL) was carried out prior to conducting the kinetic study and did not show any activity, nor did homogeneous combustion of propane occur. The diagnostic test of external and internal mass transfer limitations were also carried out prior to conducting the kinetic study and show that the reaction was free of external and internal mass transfer limitations. The effect of external intra-particle mass transfer and external film diffusion was avoided on the oxidation reaction by using fine particle (100-150 mesh) of the catalyst. To be on the safe side, the catalyst with the smaller particle size was used for collecting the kinetic data.

The kinetic data of the oxidation of C₃H₈ over the NiCo₂O₄ catalyst at different temperatures is presented in Figure 1. The oxygen in the reaction mixture was in too much excess and hence the variation in its concentration due to the oxidation was negligible. Efforts were made to fit the kinetic data to power law rate expression as preferred by Levenspiel [23].

3.1. Kinetics of propane oxidation over NiCo₂O₄ catalyst

Meaningful kinetic data can be obtained from a packed bed reactor, only if the flow pattern within the reactor resembles plug flow. Plug flow behavior provides a simple relationship between feed rate and the rate of reaction. Since the ratios of the length and diameter of the reactor to particle size used in the present exceed 30 and 6, respectively, it can be safely assumed that the flow in the packed bed reactor satisfies the conditions for plug flow to exist

in the reactor. The reactor to particle diameter ratio of 20-30 can be more than adequate to assume a flat velocity profile across the reactor diameter. The catalyst bed length to particle diameter ratio of 50-80 allows one to neglect the axial dispersion in the catalyst bed. In this study, these conditions have been sufficiently satisfied and it implies that the reactor used behaving as an ideal plug flow reactor. Therefore, the rate of C₃H₈ oxidation in the plug flow reactor can be given as Equation 2.

$$-r_P = dX_P/d(W/F_{P0}) \quad (2)$$

where, X_P is conversion of propane and W/F_{P0} is the weight hourly space velocity (WHSV).

A number of runs in the packed bed were performed applying various values of the WHSV. Variation in W/F_{AO} was made by changing either catalyst weight or feed rate of propane and keeping the other parameters constant. To minimize the heat and mass transfer effects and to attain approximately the behavior of the differential reactor, the upper limit of propane conversion for each run was restricted to 50%. The rate of reaction at any conversion can be obtained by measuring the slope on the curve, which was obtained by plotting X_P versus W/F_{P0} values as shown in Figure 1.

Once the rate of reaction is known as a function of conversion or concentration of reactant, an empirical power law type Equation 3 can be fitted.

$$-r_P = k (C_P)^n (C_{O_2})^m \quad (3)$$

where, k is reaction rate constant and C_P is concentration of propane and C_{O₂} is the concentration of the oxygen. In the present study a lean mixture of reactant, 2.5 % propane in air, was used, therefore oxygen was in large excess and the rate expression reduces to the pseudo nth order Equation 4.

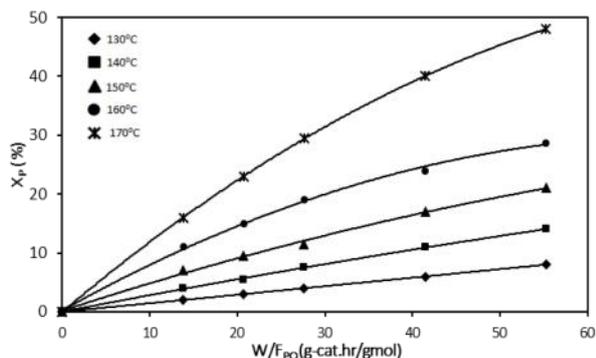


Figure 1. C₃H₈ conversion, X_P vs W/F_{P0} (gcat.h/gmol) at different temperatures

$$-r_P = k(C_P)^n \quad (4)$$

$$\text{or } \ln(-r_P) = \ln k + n \ln C_P \quad (5)$$

The data of the fractional conversion of X_P versus W/F_{P0} at five different temperatures is shown in Figure 1. Rate of reaction (-r_P) at different degree of conversion for each temperature were determined by measuring the slopes of the curves. It may be noted that the reactant mixture was lean (2.5%) and therefore, the changes taking place in volume due to the reaction can be neglected without introducing any significant error. Therefore, we assume constant density system due to negligible value of variable density factor. Under this condition, the following expressions in Equation 6 is valid:

$$C_P = C_{P(\text{inlet})}(1-X_P) \quad (6)$$

where, C_{P(inlet)} and C_P are concentration of propane at inlet and at outlet of reactor respectively. The C_{P(inlet)} can be calculated assuming ideal gas law then C_P was determined using Equation 6.

If the power law is valid and -r_P versus C_P data are known at constant temperature, n and k at that temperature can be determined from plot of ln(-r_P) versus ln(C_P). In the entire cases plots were found to be linear (Figure 2). The kinetic parameters (k and n) of the power law model for the combustion of propane were determined from slope and intercept of the plot (Figure 2). Order of the reaction was found to be 0.53.

The rate constant, k, is a function of temperature and can be expressed by Arrhenius Equation 7.

$$k = A \exp(-E/RT) \quad (7)$$

$$\text{or } \ln k = \ln A - E/RT \quad (8)$$

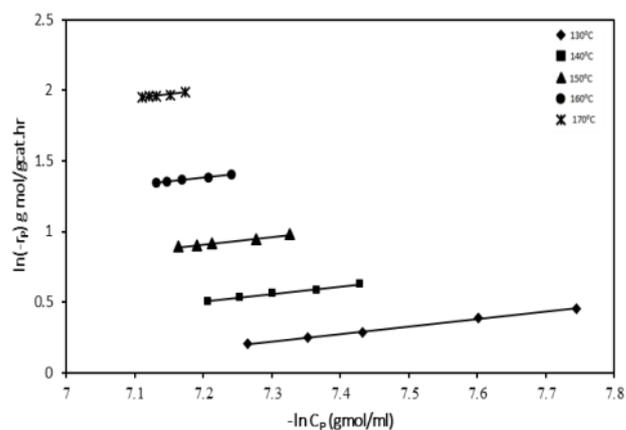


Figure 2. Plot of ln(-r_P) vs ln C_P

The activation energy (E) of the reaction can be evaluated from the slope of the plot of $\ln(k)$ versus $1/T$ as per Equation 8. Linear plot was obtained when $\ln k$ vs. $1/T$ was plotted (Figure 3).

The activation energy and pre-exponential factor (A) of Arrhenius equation thus determined are given below:

$$E = 14.28 \text{ kcal/gmol} = 59.3 \text{ kJ/gmol} \quad (9)$$

$$A = 2.9 \times 10^8 \text{ (gmol)}^{0.47} \cdot \text{L}^{0.53} / \text{(gcat.h)} \quad (10)$$

On the basis of the experimental findings the rate of propane oxidation ($-r_p$, in gmol/gcat.h) in the temperature ranges of 130-170 °C on the NiCo_2O_4 catalyst can be expressed as follows:

$$-r_p = 2.9 \times 10^8 \exp(-14284/RT)(C_p)^{0.53} \quad (11)$$

The above empirical rate expression can be adequately used for the design of catalytic converter used in LPG fuelled vehicles.

4. Conclusions

The present work is given phenomenological frame to understand the action of NiCo_2O_4 catalyst in propane oxidation reaction. The oxidation of propane is studied in a fixed bed plug flow reactor and kinetics data are collected under the condition of free heat and mass transfer limitations. Intrinsic rate of air oxidation of propane over NiCo_2O_4 catalyst is determined as a function of temperature and concentration in the temperature range of 130-170 °C. The rate of propane oxidation (gmol/gcat.h) is given by: $-r_p = 2.9 \times 10^8 \exp(-14284/RT)(C_p)^{0.53}$. The value of activation energy is found to be 59.3 kJ/mol, which is the least compared with activation energy for different catalysts reported in the literature for propane oxidation. The obtained kinetics expression can be implemented into CFD models for reactor design and optimization of parameters.

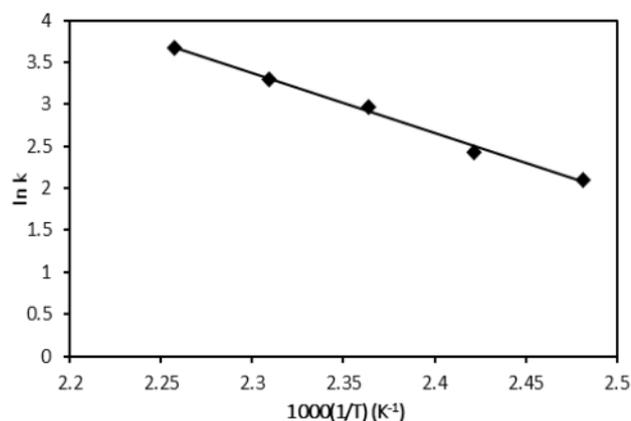


Figure 3. Arrhenius plot

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