Kinetics of the Complete Combustion of Dilute Propane over Mn-doped ZrO₂ (cubic) Catalyst

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Abstract: *Kinetics of the complete combustion of propane at very low concentration in air (0.45 mole % in air) over Mn-doped ZrO₂ (cubic) catalyst (Mn/Zr=0.25) at different temperatures (573-673 K) in kinetic control regime have been investigated. The activation energy and frequency factor for the combustion were found to be 20.14 kcal. mol^{-1} and 2.38×10^5 $mol..g^{-1}.h^{-1}.kPa^{-0.5}$, respectively.*

Key Words: *Kinetics of propane combustion, Mn- doped ZrO₂ (cubic) catalyst, complete combustion.*

1. Introduction

The release of higher hydrocarbons in the atmosphere also affects the environment because of their toxicity and/or photochemical reactions with NO_X and other air-borne chemicals, causing a photochemical smog. Hence it is necessary to avoid the emissions of higher hydrocarbons, such as propane and butanes (present in the exhaust gases of LPG fueled engines) and hydrocarbon solvents (e.g. toluene and xylenes) used in the chemical and processing industries, by their complete combustion.

A few studies have been reported on the kinetics of catalytic propane combustion. The propane combustion over Pt/Al_2O_3 catalyst could be described very well by Langmuir-Hinshelwood model, in which molecularly adsorbed hydrocarbon reacts with dissociatively adsorbed oxygen (2-7). Interestingly, for the $La_{0.66}$ $Sr_{0.34}$ $Ni_{0.3}$ $Co_{0.7}$ O_3 perovskite oxide catalyst, the best fit for the propane combustion data (8) was obtained with the Mars-van Krevelen kinetic model (9-11).

Power law model was also employed for fitting propane combustion kinetic data. For the propane combustion over Pt/Al_2O_3 (3, 12), the reaction order for the fuel lean conditions was found to be 1.1 for propane and – 0.6 for oxygen (3) and 0.4 for propane and – 0.9 for oxygen (12). For the combustion of propane over $La_{0.66}$ $Sr_{0.34}$ $Ni_{0.3}$ $Co_{0.7}$ O_3 catalyst, the reaction order was 0.5 and 0.3 with respect to propane and oxygen, respectively, (8).

Whereas, anomalous reaction orders, -2.9 for oxygen and 3.4 for propane were observed for the combustion of propane over Pt/ZrO_2. (13).

Although, the noble metal based catalysts are more active than the transition metal oxide(s)-based catalysts in the complete combustion of hydrocarbons (1,14) and volatile organic compounds (15,16,17), the former are very costly, more prone to sulfur poisoning and also thermally less stable. Hence, constant efforts are being made world wide to develop transition metal oxide(s)-based catalysts having combustion activity comparable to that of the noble metal catalysts (1). It is therefore interesting to study in details the kinetics of the combustion of propane over this catalyst.

The present work was undertaken with the objective of studying the kinetics of the complete combustion of dilute propane (0.45 mol % in air) over the Mn-doped ZrO₂ (cubic) catalyst at different temperatures (573- 673 K). Efforts have been made to fit the combustion rate data to power law, redox (Mars-van Krevelen) and Eley-Rideal rate models.

2. Experimental

The Mn-doped ZrO₂ (cubic) catalyst was prepared by co-precipitating mixed Zr and Mn hydroxides from mixed aqueous solution of zirconyl nitrate and manganese acetate, with Mn/Zr ratio of 0.25, using the precipitating agent tetramethyl ammonium hydroxide (25%) (TMAOH) under vigorous stirring at the room temperature (300 K) and a pH of 8, washing (with deionized water) and drying (at 382 K for 2 h) the resulting precipitate and then calcining it in air at 773 K for 8 h. The calcined mass was powdered, palletized without binder and crushed to 100-120 mesh size particles. The characterization of the catalyst by XRD, temperature programmed reduction and XPS has been given earlier (19).

The catalytic combustion of propane (0.45 mole % in air) over the Mn-doped ZrO₂ catalyst was carried out at atmospheric pressure in a continuous fixed bed quartz

micro-reactor (i.d. 10 mm) containing 0.1 g catalyst (100-120 mesh size particles) mixed uniformly with 0.4 g inert α-alumina particles (100-120 mesh size) at different temperatures (573-673 K) and space velocities (25,000-1,50,000 $cm^3.g^{-1}.h^{-1}$). The space velocity was measured at 273 K and 1 atm pressure. The air diluted propane feed was obtained by mixing the premeasured methane and air streams in a long stainless steel coiled tube (i. d. 2 mm and length 3 m) The flow rates of both the streams were controlled using digital differential pressure flow controllers (the air used was zero grade, free from moisture and hydrocarbons). The reaction temperature was measured by a Chromel-Alumel thermocouple located in the catalyst bed. The products (after cooling to the room temperature) were analysed by an online gas chromatograph with thermal conductivity and flame ionization detectors, using poropack-Q column (with TCD) for the analysis of CO and CO_2 and SE-30 column for the analysis of unreacted propane and the partial oxidation products. Under the reaction conditions employed in the present work, no formation of carbon monoxide and other partial oxidation products (oxygenates) in the combustion of propane was detected.

3.   Results and Discussion

3.1 Catalyst Characterization. The Mn-doped ZrO_2 catalyst has been characterized in our earlier studies (18). The catalyst properties are given in Table 1. The observation of the single ZrO_2 (cubic) crystalline phase and the low degree of MnO_2 reduction indicated a complete doping of Mn in the ZrO_2.

Table 1. Bulk and Surface properties of the Mn-doped ZrO_2 catalyst

Crystalline phase	ZrO_2 (cubic)
Surface area	105 $m^2.g^{-1}$
Oxidation state of Mn	Mn (IV)
Degree of catalyst reduction (2 MnO_2 + H_2 → Mn_2O_3 + H_2O)	10.5 %

3.2 Fittings of Kinetic Data. The kinetic data for the complete combustion of propane (0.45 mole percent in air)

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (1)$$
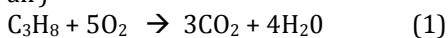
over the Mn- doped ZrO_2 catalyst at different temperatures is presented in Fig.1. The W/F is based on total flow of the gases in the feed. The kinetic data were collected in the absence of heat and mass transfer effects, as follows. In

order to avoid the formation of hot spots in the catalytic bed, the catalyst was diluted with the inert solid particles (diluent/catalyst weight ratio=4), so that the heat transfer area of the catalyst bed is increased. When undiluted catalyst was used, a higher conversion was observed. An increase in the diluent/catalyst ratio from 4 to 6 had no significant effect on the conversion. Influence of the external film diffusion and intra-particle mass transfer on the combustion was eliminated by using fine particles of the catalyst (particle size= 100-120 mesh). An increase in the catalyst particle size from 100-120 to 60-80 mesh size had no significant effect on the conversion (at the highest temperature). To be on the safe side, the catalyst with the smaller particle size was used for collecting the kinetic data.

The X versus W/F curves (Fig.1) were fitted to the following expression,

$$X = a + b(W/F) + c(W/F)^2 + d(W/F)^3 \qquad (2)$$

by linear regression method. On the differentiation with respect to W/F of eqn.2, we get

$$dX/d(W/F) = \text{rate of combustion} = b + 2c\ (W/F) + 3d\ (W/F)^2 \qquad (3)$$

where, $dX/d(W/F)$ is the rate of combustion.
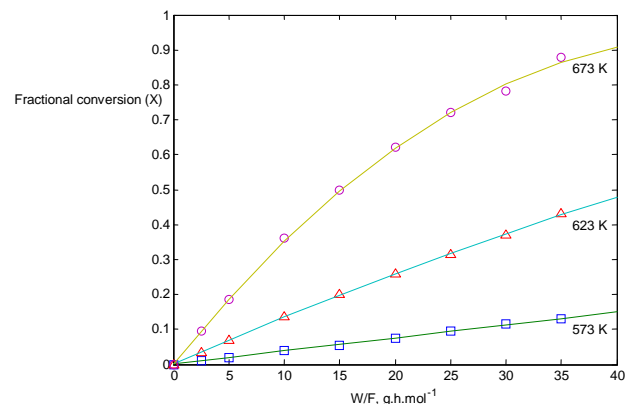

Figure 1: Conversion versus W/F plots for the combustion of propane at different
        temperatures

The kinetic rate data (reaction rate at different partial pressures of the hydrocarbons) have been obtained from eqn. (3) and the fractional conversion at the respective W/F (Fig.1). The oxygen in the reaction mixture was in too much excess and hence the variation in its concentration due to the combustion was quite small.

Efforts were made to fit the kinetic data to the power law, redox (Mars-van Krevelen) and Eley-Rideal rate models, as follows.

Power Law Rate Model

The kinetic data for the combustion of propane could be fitted very well to the power law model,

$$r = k P_A^n \qquad (4)$$

Where, r is the combustion rate, k is the apparent rate constant, P_A is the partial pressure of the hydrocarbon and n is the reaction order with respect to the hydrocarbon. The ln r versus ln P_A plots for all the cases were found to be linear. The kinetic parameters (k and n) of the power law model for the combustion of propane are given in Table 2.

For the propane combustion, the reaction order is increased with increasing the temperature. The mean residual sum of squares (MRSS) are very small (Table 2), indicating a very good fit of the kinetic data to the power law model.

Temperature T (K)	Rate constant k (mol.g^{-1}.h^{-1}.kPa^{-n})	Reaction order N	Residual sum of square (RSS)[a]	Mean residual sum of square (MRSS)[b]
573	0.005	0.31	2.53×10^{-11}	3.17×10^{-12}
623	0.021	0.50	2.41×10^{-9}	3.01×10^{-10}
673	0.068	0.64	4.97×10^{-6}	6.21×10^{-7}

Table 2. Kinetic parameters of the power law model for the combustion of propane

[a] RSS = $\Sigma[r(observed)-r(estimated)]^2$
[b] MRSS = $\Sigma[r(observed)-r(estimated)]^2/(n-1)$
  where, n=degree of freedom.

The activation energy for the combustion of propane has been obtained from the temperature dependence of k (Fig.2), according to the Arrhenius equation:
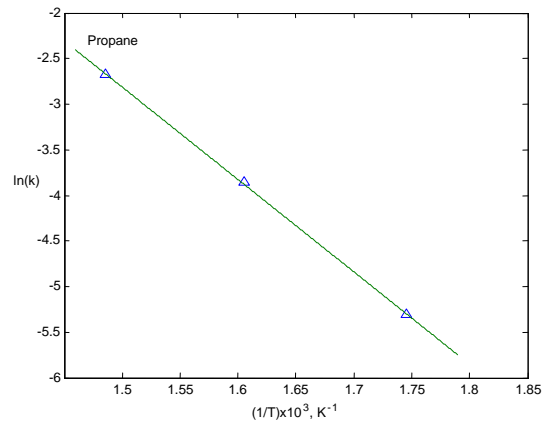
$$k = A \exp(-E/RT) \qquad (5)$$

Figure 2: Arrhenius plots (ln k versus 1/T) for the combustion of propane (for the power law model).

Where A is the frequency factor, E is the activation energy, R is the gas constant and T is the temperature. The values of the activation energy and frequency factor for the combustion of propane are given in Table 3.

Table 3. Arrhenius parameters (obtained from the power law model) for the combustion of propane

Reaction	Activation energy, E (kcal.mol^{-1})	Frequency factor, A (mol.g^{-1}.h^{-1}.kPa^{-n})
Propane combustion	20.14	2.38×10^5

Redox (Mars-van Krevelen) Rate Model

The redox model of Mars-van Krevelen for catalytic hydrocarbon oxidation reactions (14) involves following two irreversible steps, operating in the cyclic manner: first, the reaction of hydrocarbon with the lattice oxygen of the catalyst leading to the formation of oxidation products and the reduction of the metal oxide in the catalyst, and second the reoxidation of the reduced metal oxide by the oxygen present in the feed. The overall rate of the hydrocarbon oxidation can be expressed by the redox expression,

$$r = k_1 k_2 P_A P_{O_2}/(k_1 P_{O_2} + k_2 \gamma P_A) \qquad (6)$$

or

$$P_{O_2}/r = (1/k_2)(P_{O_2}/P_A) + (\gamma/k_1) \qquad (7)$$

Where, k_1 is the rate constant for the reoxidation of the catalyst, k_2 is the rate constant for the oxidation of propane by the lattice oxygen and γ is the stoichiometric coefficient

for oxygen in the combustion ($\gamma = 5$ for the combustion of propane).

Linear plots of P_{O_2}/r versus P_{O_2}/P_A (P_A = partial pressure of propane) for the combustion of propane in Fig.3 shows that the combustion of propane follows the redox mechanism.
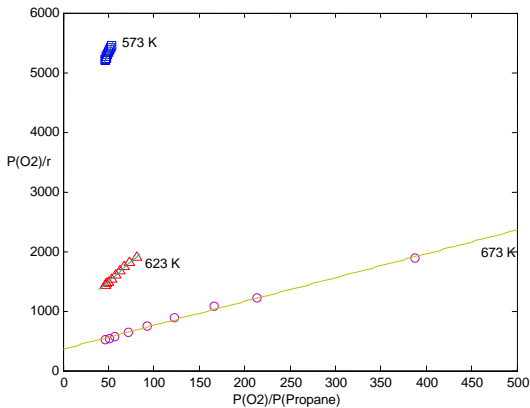

Figure 3: Redox model plots (P_{O_2}/r versus $P_{O_2}/P_{propane}$) for the combustion of propane.

Values of the rate constants, k_1 and k_2, along with the residual sum of squares and mean residual sum of squares at the different temperatures for the combustion of the propane are given in Table 4.

Table 4. Kinetic parameters of the redox (Mars-van Krevelen) model for the combustion of propane

Temperature T (K)	Rate constant (mol.g^{-1}.h^{-1}.kPa^{-1})		Residual sum of square (RSS)	Mean residual sum of square (MRSS)
	k_1	k_2		
573	0.0014	0.0295	4.08×10^{-11}	5.10×10^{-12}
623	0.0061	0.0746	2.30×10^{-8}	2.87×10^{-9}
673	0.0139	0.2502	1.19×10^{-5}	1.49×10^{-6}

Figure 4 shows the temperature dependence of the rate constants (k_1 and k_2) of the redox model, according to the Arrehenius equation, for the combustion of propane. The values of the Arrhenius parameters (activation energy and frequency factor) for the combustion of propane, obtained from the linear Arrhenius plots (Fig.4) are given in Table 5
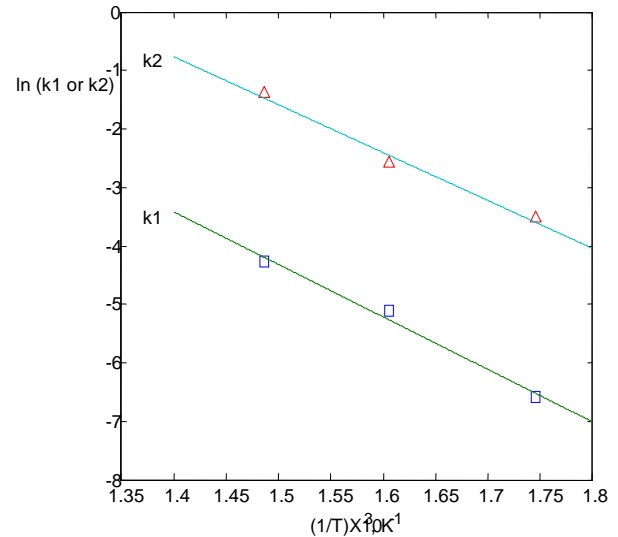

Figure 4: Arrhenius plots (ln k_1 or k_2 versus 1/T) For the combustion of propane (for the redox model).

Table 5. Arrhenius parameters (obtained from The redox (Mars-van Krevelen) model) for the combustion of propane

Reaction	Activation energy (kcal.mol^{-1})		Frequency factor, (mol.g^{-1}.h^{-1}.kPa^{-1})	
	E_1	E_2	A_1	A_2
Propane combustion	17.86	16.31	9.44×10^3	4.50×10^4
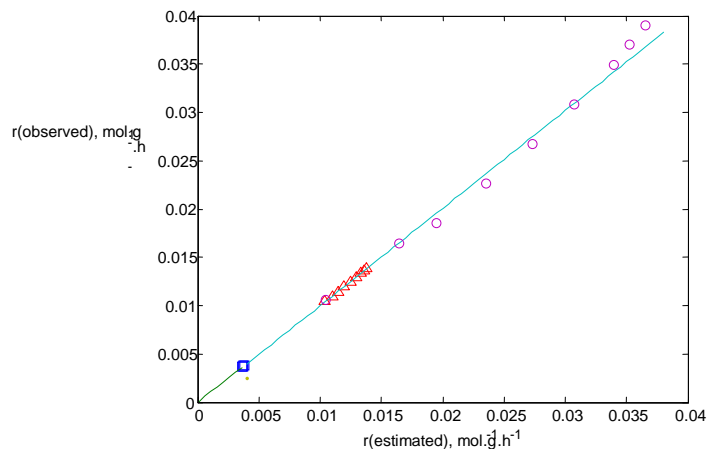
Figure 5: $r_{observed}$ versus $r_{estimated}$ (redox model) for the combustion of propane (□-573 K,△- 623 K and 0- 673 K).

The $r_{observed}$ versus $r_{estimated}$ (from the redox model, eqn. 7) plot in Fig. 5 for the combustion of propane clearly

shows an excellent fit of the kinetic data to the redox model. However, a comparison of RSS and MRSS data for the redox model (Table 4) with that for the power law model (Table 2) indicates that the power law model provides a better fit to the kinetic data for the combustion of propane at all the temperatures studied.

Eley-Rideal Rate Model

When the combustion rate data were fitted to the Eley-Rideal model (10),

$r = (k_r \, Ko_2 \, Po_2 \, P_A) / (1 + Ko_2 \, Po_2)$ (8)

both the reaction rate constant (k_r) and oxygen adsorption constant (Ko_2) at all the temperatures have been found to have negative values. Hence, in the neither case the combustion follows the Eley-Rideal mechanism.

Conclusions

The rate data for the complete combustion of propane (at very low concentration in air) over the Mn-doped ZrO_2 (cubic) catalyst could be fitted very well to both the power law and redox (Mars-van Krevelen) models. However, the power law model provides a better fit to the rate data for the combustion of propane at all the temperatures studied.

Acknowledgement

Nomenclature

Notations
A = frequency factor (mol.g^{-1}.h^{-1}kPa^{-n})
E = activation energy (kcal.mol^{-1})
F = flow rate of propane (mol.h^{-1})
k = apparent rate constant (mol.g^{-1}.h^{-1}.kPa^{-n})
k_1 = rate constant for reoxidation of catalyst (mol.g^{-1}.h^{-1}.kPa^{-1})
k_2 = rate constant for the oxidation of propane by lattice oxygen (mol.g^{-1}.h^{-1}.kPa^{-1})
k_r = reaction rate constant (mol.g^{-1}.h^{-1}.kPa^{-1})
Ko_2 = oxygen adsorption constant (kPa^{-1})
n = reaction order with respect to hydrocarbon
P_A = partial pressure of propane (kPa)
Po_2 = partial pressure of oxygen (kPa)
R = gas constant (cal.g^{-1}.mol^{-1})
r = combustion rate (mol.g^{-1}.h^{-1})
T = temperature (K)
W = weight of catalyst (gm)
X = fractional conversion
Greek Letters
γ = stoichiometric coefficient of oxygen in the combustion

Subscripts
A = propane
O_2 = oxygen

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