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Reaction kinetics of ethane partial oxidation to acetic acid

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Abstract

The partial oxidation of ethane to ethylene and acetic acid on supported MoVNbPd/TiO₂ (P25 of Degussa) has been investigated. Pd was added in a nano-metallic form. The catalyst composition was also different from similar studied catalysts. This results in a better selectivity towards acetic acid formation. The reaction was carried out in a tubular reactor at temperature range 225–275 °C, total pressure range 0–200 psig and oxygen percentage in the feed gas of 10–40%. The feed gas contains ethane and oxygen. In this work, we develop a kinetic model for the reaction for the developed catalyst. In this model, we assume that oxidation reactions take place on different sites; ethane oxidation takes place on one site, ethylene oxidation on another site, and CO is oxidized to CO₂ on a third site. The model exhibits good agreement with the experimental data.

Keywords Ethane · Ethylene · Acetic acid · Partial oxidation · MoVNbPd catalyst

Introduction

Acetic acid is mainly produced industrially on large scale from methanol carbonylation which accounts for 65% of world capacity, but gives rise to many problems, such as corrosion and waste disposal. Other processes include acetaldehyde oxidation and ethane partial oxidation. A plant for partial oxidation of ethane to acetic acid is operated by SABIC of Saudi Arabia since 2005. Vinegar which is about 4–6% diluted form of acetic acid is obtained by fermentation of renewable carbon sources containing ethanol. Acetic acid is primarily used in the production of vinyl acetate monomer (VAM), acetic anhydride and as a solvent in the production of terephthalic acid (TPA).

MoVNb catalysts were shown [1] to be able to effect the partial oxidation of ethane to ethylene and acetic acid. The

addition of Pd makes the catalyst more selective towards acetic acid formation.

The design of industrial reactors for partial oxidation of ethane over MoVNbPd catalyst requires a reliable kinetic model. In this paper we attempt to obtain kinetic expression for ethane partial oxidation based on known mechanisms that are usually used in partial oxidation reactions.

The following three mechanisms are usually used in partial oxidation reactions;

1. Langmuir–Hinshelwood (LH) in which the adsorbed oxygen and adsorbed ethane on the active sites of the catalyst react in the adsorbed states,
2. Eley–Rideal (ER) in which one of the reactants is adsorbed and react in the adsorbed state with the other reactant in the gas phase.
3. Mars–Van Krevelen redox (MvK) in which the oxidized catalyst react with ethane and thus is reduced and is reoxidized with molecular oxygen.

In the pioneering work of Thorsteinson et al. Mo–V–Nb catalysts [1], have been reported as active for the partial oxidation of ethane to ethylene and acetic acid using oxygen. In their work the kinetics for Mo₁₆V₈Nb_{2,29} was derived assuming LH mechanism. Two schemes have been suggested to explain the mechanism. In one scheme, ethoxy–hydroxyl species are formed and these decompose to ethylene. In the second scheme a hydroxy–alkoxy is formed and this

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decomposes to ethylene and water. Bare metal sites M reacts with water to form MOH which reacts with ethylene to give an ethoxide MOC_2H_5 . The ethoxide is oxidized to acetic acid.

For acetic acid production, a pressure of about 300 psig gives acetic acid selectivity about 20%, and ethylene selectivity about 70%. In addition, the use of high pressure is advantageous in reducing contact time for a specified ethane conversion and thus reducing the catalytic reactor bed.

To avoid the formation of inflammable mixture, the feed to the reactor contains low percentage of oxygen limiting ethane conversion. This requires the recycle of unreacted ethane.

The kinetics of Thorsteinson et al. has been used for simulation of fixed bed reactor [2], and fluidized bed reactor [3]. To avoid the formation of inflammable mixture, El-Sherehy et al. [4] studied the use of distributed oxygen along the reactor bed.

Karim et al. [5] showed that the addition of Pd to the MoVNb catalyst greatly increases the selectivity to acetic acid to about 80% and completely oxidizes CO to CO_2 .

Fakeeha et al. [6] obtained the kinetics for MoVPO catalyst. A model based on Eley–Rideal and Mars and Van Krevelen redox mechanisms were found adequate.

The mechanism and kinetics of the reaction with a $Mo_1V_{0.25}Nb_{0.12}Pd_{0.0005}O_x$ catalyst were studied by Linke et al. [7, 8]. It has been shown that ethylene inhibits ethane oxidation through depletion of lattice oxygen (O^*). The consecutive oxidation of ethylene to acetic acid is itself catalyzed by the palladium oxide in a heterogeneous analogue of the Wacker process.

Their kinetic model contains some negative activation energy which is physically wrong. They have indicated that the C–H bond activation in ethane by the oxygen-saturated catalyst surfaces is the rate limiting step [7]. Water is also believed to increase acetic acid selectivity by promoting the desorption of acetate species as acetic acid [7].

The kinetics of MoV type catalyst was re-investigated by Rahman et al. [9] but the catalyst composition was not mentioned. Most probably it contains Nb and Pd. Rahman et al. [9] developed a two-site Eley–Rideal–Redox (ERR) model to predict the partial oxidation of ethane to ethylene and the partial ethane oxidation to acetic acid over the catalyst. To be used in acetic acid plant design, we need to know how much CO is produced. However, their model assumes that the oxidation of ethylene and acetic acid to CO is insignificant. Also the oxidation of ethane to CO and CO_2 is negligible.

Li and Iglesia [10, 11] found that precipitation of Mo, V and Nb salts solution in the presence of colloidal TiO_2 (titania P25 from Degussa) led to a tenfold increase in ethylene and acetic acid rates (per active oxide) without significant changes in selectivity relative to unsupported samples. The introduction of trace amounts of Pd

(0.0025–0.01 wt%) as a physical mixture of separate 0.3 (wt%) Pd/SiO₂ led to the near complete depletion of ethylene and to a significant increase in acetic acid synthesis rate.

A suitable kinetic model for the catalytic oxidation of ethane to acetic acid on MoVNb catalyst must be able to explain the following key observations:

1. Rate of depletion of ethane is first order with respect to ethane as noted by Thorsteinson et al. [1]. Burch and Swarnakar [12] determined the rate of reaction to be 0.8–1.0 with respect to ethane depending on temperature.
2. Rate of depletion of ethane is a fraction close to zero with respect to oxygen as noted by Thorsteinson et al. [1]. Burch and Swarnakar [12] determined the rate of reaction to be 0.07–0.5 with respect to oxygen.
3. High pressure favors the formation of acetic acid.
4. Temperature increase makes the reaction more selective to ethylene with respect to acetic acid.
5. The strong acceleration of the rate of the ethylene oxidation to acetic acid by the presence of water (Linke et al. [7, 8]; Rahman et al. [9]). Water, whether formed as a byproduct or added with $C_2H_6-O_2$ reactants, increases acetic acid selectivity by promoting the desorption of adsorbed acetate species as acetic acid. Thus, the promoting effect of water on acetic acid selectivity reflects a specific increase in the rate at which ethane converts to acetic acid via direct pathways. The absence of water led to larger (ethylene/acetic acid) ratios in products and to slightly higher CO_x selectivity.
6. Palladium catalyzes the oxidation of CO to CO_2 . Berlowitz et al. [13] have shown that for some range of operating conditions the rate of CO oxidation is first order in oxygen and negative first order in CO.

The catalyst used in our experiments has the composition $Mo_{16}V_{6.37}Nb_{2.05}O_xPd_{0.0037}/TiO_2$ (P25). The catalyst loading on Titania is 30%. Pd was added. The method of preparation, catalyst characterization and the effect of operating parameters for the partial oxidation reaction of ethane such as temperature, space time and feed composition are described in references [15, 16]. The experimental tubular reactor used to carry out the experiments is also described in these two references. This catalyst composition was optimized for maximum acetic acid yield, and thus it is required to develop a kinetic model for its use in the partial oxidation reaction of ethane to acetic acid.

In the next section, the experiments carried out and the results are presented. This is followed by the kinetic model suggested. Parameter estimation results are then presented. The results are then discussed and reaction mechanism is suggested. Finally, conclusions are presented.

Experimental

The reaction system set up is described in Ref. [16]. Briefly 0.3 g of the catalyst diluted with silica particles of the same size is placed in the reactor tube of overall length 150 mm with inside diameter of made of 6.35 mm stainless steel and surrounded by brass block. The block is surrounded by mica band heater.

At the beginning of the experiments, we tested the effect of reducing the catalyst particle size on ethane conversion. No noticeable change happened. We concluded that intraparticle mass transfer is negligibly small.

For the present kinetic study sixty-three experiments were carried out for ethane oxidation. Temperatures varied between 225 and 275 °C, pressures from atmospheric to 200 psig, total gas inlet flow-rate containing ethane and oxygen from 10 to 40 ml/min, and O₂% in the feed between 10 and 40. In all experiments, catalyst weight was 0.3 g. Specifically, the following experiments were carried out:

- At pressure 200 psig, and flow-rate 10 ml/min;
 - One experiment at 225 °C and 10% O₂
 - Two experiments at 225, 240 °C and 20% O₂
 - One experiment at 225 °C and 40% O₂
- At pressure 200 psig, and flow-rate 20 ml/min;
 - Two experiments at 225, 240 °C and 10% O₂
 - Three experiments at 225, 240, 250 °C and 20% O₂
 - Three experiments at 225, 250, 275 °C and 40% O₂
- At pressure 200 psig and flow-rate 40 ml/min
 - Two experiments at 225, 250 °C and 10% O₂
 - Four experiments at 225, 250 °C and 20 and 40% O₂
- At pressure 100 psig and flow-rate 10 ml/min
 - One experiment at 225 °C and 10% O₂
 - Two experiments at 225, 250 °C and 20% O₂
 - Three experiments at 225, 250, 275 °C and 40% O₂
- At pressure 100 psig and flow-rate 20 ml/min,
 - One experiment at 225 °C and 10% O₂
 - Two experiments at 225, 250 °C and 40% O₂.
- At pressure 100 psig and flow-rate 40 ml/min, nine experiments at 225, 250, 275 °C and 10, 20 and 40% O₂.
- At pressure 0 psig, twenty-seven experiments at 225, 250, 275 °C and 10, 20 and 40% O₂, flow-rates of 10, 20 and 40 ml/min.

The results are shown in Table 1.

Some observations can be made from testing results:

- Acetic acid is not formed at atmospheric pressure.

- Ethylene is the primary product at low temperature and low pressure.
- Ethylene selectivity decreases with the increase of temperature.
- Acetic acid is the primary product at high pressure and low temperature.
- In all experiments the selectivity of CO was very low.
- The selectivity of CO₂ increases with the increase of temperature and the increase in O₂% in the feed.
- The pressure range for the experiments is very wide with high selectivity to ethylene and CO₂ at low pressure and high selectivity to acetic acid at high pressure. It would be a challenge to find a model that is suitable for wide variation in the pressure.

Kinetic modeling of partial oxidation of ethane

Here we attempt to obtain kinetic expression based on known mechanisms that are usually used in partial oxidation reactions. These are Langmuir–Hinshelwood (LH) kinetics assuming reaction taking place between adsorbed species, Eley–Rideal kinetics assuming reaction taking place between adsorbed species and gaseous reactant, and Mars–Van Krevelen redox mechanism in which the oxidized catalyst react with ethane and thus is reduced and is reoxidized with molecular oxygen.

For the reaction



where A could be a hydrocarbon and B is the corresponding dehydrogenated hydrocarbon.

Langmuir–Hinshelwood kinetics takes the form

$$\text{Rate of oxidation reaction} = \frac{kP_A^{m_1}P_{O_2}^{m_2}}{[1 + K_1P_{O_2} + K_2P_A + K_3P_B + K_4P_w]^{m_3}}. \quad (2)$$

While the redox kinetics take the form

$$\text{Rate of oxidation reaction} = \frac{kP_AP_{O_2}}{P_{O_2} + KP_A}. \quad (3)$$

The reaction network is assumed in its most general form of Fig. 1 (r_i 's denote reaction rates of different species).

This assumes that acetic acid can be obtained from ethane and ethylene and that all reactants and products are oxidized to CO and CO₂ and CO is converted to CO₂.

We assume the conversion of ethane is X_1 , the conversion to CO is X_2 , CO₂ is X_3 , and CH₃COOH is X_4 . In

Table 1 Results of kinetic study

Pressure psig	Flow ccm/min	O ₂ In feed %	Temp. °C	O ₂ conv. %	C ₂ H ₆ conv. %	Selectivity (%)				Space time yield gm/kg h	
						Ethylene	Acetic acid	CO	CO ₂	Acetic acid	Ethylene
200	10	10	225	99.49	4.04	2.06	82.79	0.00	15.15	161.26	1.87
200	10	20	225	74.98	6.37	1.08	83.81	0.31	14.8	228.80	1.38
200	10	20	240	99.32	9.25	0.37	81.79	0.09	17.74	324.23	0.69
200	10	40	225	42.68	9.52	0.83	77.01	0.28	21.88	235.64	1.19
200	20	10	225	66.09	3.26	6.71	77.84	0.67	14.78	244.69	9.84
200	20	10	240	99.42	4.89	4.08	79.47	0.4	16.05	374.72	8.98
200	20	20	225	42.09	4.80	2.62	81.76	0.47	15.15	336.38	5.03
200	20	20	240	72.71	7.31	1.43	79.75	0.32	18.50	499.68	4.18
200	20	20	250	97.16	9.56	0.82	78.82	0.22	20.15	645.86	3.14
200	20	40	225	24.31	6.44	2.59	82.00	0.56	14.85	339.47	5.00
200	20	40	250	62.54	15.18	0.73	71.2	0.23	27.84	694.79	3.32
200	20	40	275	99.94	21.96	0.15	64.64	0.16	35.06	912.51	0.99
200	40	10	225	30.68	1.78	12.76	71.61	1.32	14.32	245.82	20.44
200	40	10	250	79.12	3.50	4.99	76.65	0.52	17.84	517.37	15.72
200	40	20	225	17.12	2.21	10.29	76.17	1.36	12.18	288.57	18.19
200	40	20	250	49.97	6.12	2.67	78.79	0.54	18.00	826.60	13.07
200	40	40	225	12.21	3.01	6.99	74.77	1.26	16.99	289.35	12.62
200	40	40	250	27.21	7.93	2.44	74.1	0.59	22.88	755.48	11.61
100	10	10	225	75.53	2.88	2.30	82.83	0.15	14.718	115.01	1.49
100	10	20	225	43.54	4.53	1.95	81.9	0.17	15.98	159.00	1.77
100	10	20	250	99.04	11.08	0.76	82.45	0.17	16.62	391.50	1.68
100	10	40	225	21.34	6.15	1.67	77.46	0.15	20.72	153.12	1.54
100	10	40	250	61.19	14.95	0.72	73.97	0.17	25.14	355.44	1.62
100	10	40	275	99.96	23.14	0.24	68.41	0.11	31.24	508.81	0.83
100	20	10	225	21.82	2.14	11.89	75.19	2.06	10.87	155.16	11.45
100	20	40	225	11.03	3.57	6.92	74.61	0.89	17.57	171.23	7.41
100	20	40	250	31.62	8.38	2.32	71.00	0.50	26.18	382.48	5.83
100	40	10	225	12.16	0.50	84.34	0.00	0.97	14.69	0.00	37.95
100	40	10	250	42.77	1.20	27.22	45.30	2.27	25.22	104.83	29.40
100	40	10	275	96.39	4.02	16.47	57.54	1.13	24.86	446.09	59.59
100	40	20	225	7.26	1.63	27.52	61.33	2.05	9.10	171.37	35.89
100	40	20	250	25.57	2.61	16.14	59.04	2.31	22.51	264.16	33.70
100	40	20	275	76.45	8.18	3.39	70.68	0.6	25.33	991.11	22.18
100	40	40	225	5.82	1.20	31.99	45.25	3.59	19.17	69.81	23.03
100	40	40	250	14.77	4.80	6.96	72.73	1.53	18.78	448.84	20.05
100	40	40	275	43.92	11.96	1.77	67.05	0.70	30.48	1031.01	12.70
0	10	10	225	15.25	0.98	100.00	0.00	0.00	0.00	0.00	22.05
0	10	10	250	41.76	1.98	86.15	0.00	2.54	11.31	0.00	38.38
0	10	10	275	90.01	3.56	58.51	0.00	6.89	34.60	0.00	46.87
0	10	20	225	8.35	1.01	100.00	0.00	0.00	0.00	0.00	20.20
0	10	20	250	21.85	2.02	80.07	0.00	1.34	18.59	0.00	32.35
0	10	20	275	58.42	3.75	49.13	0.00	7.11	43.76	0.00	36.85
0	10	40	225	3.12	1.30	91.42	0.00	0.00	8.58	0.00	17.83
0	10	40	250	11.75	2.50	74.55	0.00	2.66	22.78	0.00	27.96
0	10	40	275	35.46	4.80	37.33	0.00	9.07	53.60	0.00	26.88
0	20	10	225	6.83	0.52	100	0.00	0.00	0.00	0.00	23.40
0	20	10	250	16.61	1.13	90.22	0.00	0.00	9.79	0.00	45.88

Table 1 (continued)

Pressure psig	Flow ccm/min	O ₂ In feed %	Temp. °C	O ₂ conv. %	C ₂ H ₆ conv. %	Selectivity (%)				Space time yield gm/kg h	
						Ethylene	Acetic acid	CO	CO ₂	Acetic acid	Ethylene
0	20	10	275	48.95	2.11	74.38	0.00	3.29	22.33	0.00	70.62
0	20	20	225	3.82	0.57	100	0.00	0.00	0.00	0.00	22.80
0	20	20	250	7.20	1.25	91.10	0.00	0.00	8.90	0.00	45.55
0	20	20	275	29.73	2.65	63.67	0.00	9.03	27.31	0.00	67.49
0	20	40	225	1.88	0.73	100	0.00	0.00	0.00	0.00	21.90
0	20	40	250	4.59	1.49	85.21	0.00	0.00	14.79	0.00	38.09
0	20	40	275	15.84	3.27	55.29	0.00	10.92	33.79	0.00	54.24
0	40	10	225	4.96	0.38	100	0.00	0.00	0.00	0.00	34.20
0	40	10	250	11.12	0.75	100	0.00	0.00	0.00	0.00	67.50
0	40	10	275	29.77	1.51	85.81	0.00	2.77	11.42	0.00	116.62
0	40	20	225	3.24	0.43	100	0.00	0.00	0.00	0.00	34.40
0	40	20	250	6.66	0.82	100	0.00	0.00	0.00	0.00	65.60
0	40	20	275	17.43	1.76	80.34	0.00	3.01	16.66	0.00	113.12
0	40	40	225	2.86	0.49	100	0.00	0.00	0.00	0.00	29.40
0	40	40	250	3.48	1.12	89.98	0.00	0.00	10.02	0.00	60.47
0	40	40	275	8.14	2.17	70.64	0.00	2.66	26.70	0.00	91.97

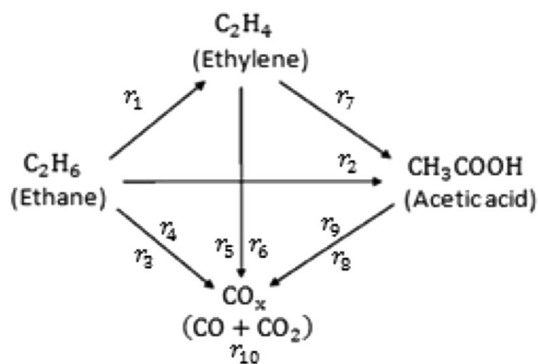


Fig. 1 Proposed scheme for ethane partial oxidation

addition, we assume that the reactor operates in the integral mode. Thus, we have

$$\tau = \frac{W}{F_{C_2H_6}} \tag{4}$$

$$\frac{dX_1}{d\tau} = r_{C_2H_6} \tag{5}$$

$$\frac{dX_2}{d\tau} = r_{CO} \tag{6}$$

$$\frac{dX_3}{d\tau} = r_{CO_2} \tag{7}$$

$$\frac{dX_4}{d\tau} = r_{CH_3COOH} \tag{8}$$

With the initial conditions at

$$\tau = \frac{W}{F_{C_2H_6}} = 0, X_1 = X_2 = X_3 = X_4 = 0, \tag{9}$$

where W = catalyst weight $F_{C_2H_6}$ = volumetric flow-rate of ethane in the feed.

The rate of depletion of ethane ($r_{C_2H_6}$) is given by

$$r_{C_2H_6} = r_1 + r_2 + \frac{1}{2}r_3 + \frac{1}{2}r_4, \tag{10}$$

where r_1 is the rate of oxidation of ethane to ethylene; r_2 is the rate of oxidation of ethane to acetic acid; r_3 is the rate of formation of CO by ethane oxidation and r_4 is the rate of formation of CO₂ by ethane oxidation.

The rate of formation of CO (r_{CO}) is given by

$$r_{CO} = r_3 + r_5 + r_8 - r_{10}, \tag{11}$$

where r_5 is the rate of formation of CO from ethylene oxidation, r_8 is the rate of formation of CO from acetic acid oxidation, and r_{10} is the rate of oxidation of CO to CO₂.

The rate of formation of CO₂ (r_{CO_2}) is given by

$$r_{CO_2} = r_4 + r_6 + r_9 + r_{10}, \tag{12}$$

where r_6 is the rate of formation of CO₂ from ethylene oxidation, and r_9 is the rate of formation of CO₂ from acetic acid oxidation, and r_{10} is the rate of oxidation of CO to CO₂.

The rate of formation of CH₃COOH (r_{CH_3COOH}) is given by

$$r_{\text{CH}_3\text{COOH}} = r_2 + r_7 - \frac{1}{2}r_8 - \frac{1}{2}r_9, \quad (13)$$

where r_7 is the rate of formation of acetic acid from ethylene.

The expressions for r_1 – r_{10} are given by

$$r_1 = \frac{k_1 \times P_{\text{C}_2\text{H}_6} \times P_{\text{O}_2}}{P_{\text{O}_2} + K_1 \times P_{\text{C}_2\text{H}_6}} \quad (14)$$

$$r_2 = \frac{k_2 \times P_{\text{C}_2\text{H}_6}^2 \times P_{\text{O}_2}^2}{(P_{\text{O}_2} + K_1 \times P_{\text{C}_2\text{H}_6})^2} \quad (15)$$

$$r_3 = \frac{k_3 \times P_{\text{C}_2\text{H}_6} \times P_{\text{O}_2}}{P_{\text{O}_2} + K_1 \times P_{\text{C}_2\text{H}_6}} \quad (16)$$

$$r_4 = \frac{k_4 \times P_{\text{C}_2\text{H}_6} \times P_{\text{O}_2}}{P_{\text{O}_2} + K_1 \times P_{\text{C}_2\text{H}_6}} \quad (17)$$

$$r_5 = \frac{k_5 \times P_{\text{C}_2\text{H}_4} \times P_{\text{O}_2}}{P_{\text{O}_2} + K_2 \times P_{\text{C}_2\text{H}_4}} \quad (18)$$

$$r_6 = \frac{k_6 \times P_{\text{C}_2\text{H}_4} \times P_{\text{O}_2}}{P_{\text{O}_2} + K_2 \times P_{\text{C}_2\text{H}_4}} \quad (19)$$

$$r_7 = \frac{k_7 \times P_{\text{C}_2\text{H}_4}^2 \times P_{\text{O}_2} \times P_{\text{H}_2\text{O}}}{P_{\text{O}_2} + K_3 \times P_{\text{C}_2\text{H}_4}} \quad (20)$$

$$r_8 = \frac{k_8 \times P_{\text{CH}_3\text{COOH}} \times P_{\text{O}_2}}{P_{\text{O}_2} + K_3 \times P_{\text{C}_2\text{H}_4}} \quad (21)$$

$$r_9 = \frac{k_9 \times P_{\text{CH}_3\text{COOH}} \times P_{\text{O}_2}}{P_{\text{O}_2} + K_3 \times P_{\text{C}_2\text{H}_4}} \quad (22)$$

$$r_{10} = \frac{k_{10} \times P_{\text{CO}} \times P_{\text{O}_2}}{(P_{\text{CO}} + K_4 P_{\text{O}_2})^2}, \quad (23)$$

with the k 's are defined as

$$k_i = k_{i,0} \times \exp\left(\frac{-E_i}{R} \left(\frac{1}{T} - \frac{1}{548.15}\right)\right), \quad (24)$$

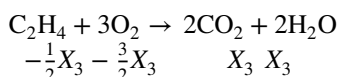
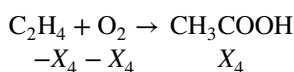
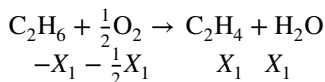
where: all pressures are in atmosphere, the rates are in $\text{Ncm}^3/\text{min g}$, k_i 's units can be deduced. K_i 's are dimensionless, E_i is activation energy in cal/mol, T is in K and $R = 1.98$ cal/

mol K. The dependence of the adsorption constants (K 's) on temperature was insignificant.

The calculated conversions are obtained by integrating equations subject to the initial condition. The pressures of the different components in terms of conversions are obtained as follows.

Let X_1 be the conversion of ethane, X_2 number of moles of CO produced per mole of ethane, X_3 number of moles of CO_2 produced per mole of ethane X_4 number of mole of CH_3COOH produced per mole of ethane.,

Y_1 moles of O_2 per mole of ethane and nt total number of moles of products per mole of ethane. Thus



$$\text{Moles of ethane} = 1 - X_1 \quad (25)$$

$$\text{Moles of oxygen} = Y_1 - \frac{1}{2}X_1 - X_2 - \frac{3}{2}X_3 - X_4 \quad (26)$$

$$\text{Moles of ethylene} = X_1 - \frac{1}{2}X_2 - \frac{1}{2}X_3 - X_4 \quad (27)$$

$$\text{Moles of CH}_3\text{COOH} = X_4 \quad (28)$$

$$\text{Moles of CO} = X_2 \quad (29)$$

$$\text{Moles of CO}_2 = X_3 \quad (30)$$

$$\text{Moles of H}_2\text{O} = X_1 + X_2 + X_3 \quad (31)$$

$$\text{Total moles (nt)} = 1 + Y_1 + \frac{1}{2}X_1 + \frac{1}{2}X_2 - X_4. \quad (32)$$

Thus, the partial pressures of the different compounds are as follows:

$$P_{\text{C}_2\text{H}_6} = \frac{(1 - X_1)}{nt} P_t \quad (33)$$

$$P_{\text{O}_2} = \frac{\left(Y_1 - \frac{1}{2}X_1 - X_2 - \frac{3}{2}X_3 - X_4\right)}{nt} P_t \quad (34)$$

$$P_{\text{C}_2\text{H}_4} = \frac{\left(X_1 - \frac{1}{2}X_2 - \frac{1}{2}X_3 - X_4\right)}{nt} P_t \quad (35)$$

$$P_{\text{CH}_3\text{COOH}} = \frac{X_4}{nt} P_t \quad (36)$$

$$P_{\text{CO}} = \frac{X_2}{nt} P_t \quad (37)$$

$$P_{\text{CO}_2} = \frac{X_3}{nt} P_t \quad (38)$$

$$P_{\text{H}_2\text{O}} = \frac{(X_1 + X_2 + X_3)}{nt} P_t \quad (39)$$

where P_t = total pressure

Parameter estimation was done by the minimization of weighted residual squares of the conversions. The resulting non-linear equations are solved by Marquardt method. The method used is described in details by Hosten et al. [14].

The computer package for carrying out estimation calculations provides statistical data. They are F value for judging goodness of fit. t values for significance of parameters

and 95% confidence regions of the parameter estimation and some others.

If the F value is small, the fit of the model is poor. At fixed number of parameters and experiments the higher is the F value the better is the fit. If a parameter is found to have very small t value, it means that it does not have a significant effect in determining the reaction rates and should be eliminated from the rate equations.

Parameter estimation results

Preliminary screening led us to conclude that the rate of oxidation of ethane to acetic acid and CO is negligibly small, i.e., $r_2 = 0$ and $r_3 = 0$. In addition, the rate of oxidation of ethylene to CO and CO₂ is negligibly small, i.e., $r_5 = 0$ and $r_6 = 0$. We obtain the following parameter estimates (Table 2).

Table 2 Parameter estimates; $F = 342.6$, residual sum of squares = 0.024

	Parameter estimate	95% Confidence		t value
		Lower limit	Upper limit	
$k_{1,0}$	1.43537	1.20362	1.66711	1.23874D + 01
$k_{2,0}$	0	n.a.	n.a.	n.a.
$k_{3,0}$	0	n.a.	n.a.	n.a.
$k_{4,0}$	1.53309	1.24128	1.82491	1.05074D + 01
$k_{5,0}$	0	n.a.	n.a.	n.a.
$k_{6,0}$	0	n.a.	n.a.	n.a.
$k_{7,0}$	1.77704D + 04	- 9.17674D + 03	4.47176D + 04	1.31891
$k_{8,0}$	4.73845D - 01	2.41522D - 01	7.06168D - 01	4.07919
$k_{9,0}$	2.09258D - 01	5.01612D - 02	3.68354D - 01	2.63057
$k_{10,0}$	2.96836D - 04	2.32607D - 04	3.61064D - 04	9.24314
E_1	1.30413D + 04	1.11920D + 04	1.48907D + 04	1.41036D + 01
E_2	n.a.	n.a.	n.a.	n.a.
E_3	n.a.	n.a.	n.a.	n.a.
E_4	2.69857D + 04	2.38892D + 04	3.00823D + 04	1.74294D + 01
E_5	n.a.	n.a.	n.a.	n.a.
E_6	n.a.	n.a.	n.a.	n.a.
E_7	1.26698D + 04	- 8.13832D + 03	3.34780D + 04	1.21778
$E_8 = E_9$	1.91947D + 03	- 6.76769D + 03	1.06066D + 04	4.41910D - 01
E_{10}	2.13033D + 04	9.87802D + 03	3.27286D + 04	3.72915
K_1	3.01309D - 01	1.96877D - 01	4.05741D - 01	5.77045
K_2	n.a.	n.a.	n.a.	n.a.
K_3	5.83161D - 01	- 1.20871D + 00	2.37504D + 00	6.50896D - 01
K_4	1.00648D - 04	7.93151D - 05	1.21982D - 04	9.43570

The values of the rate of reactions considered in this work are based on the units of normal cm³/min g They must be multiplied by 0.00268 to transform them to the more usual units of mol/h g catalyst
n.a. not applicable

Discussion

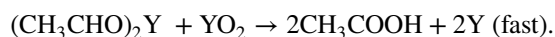
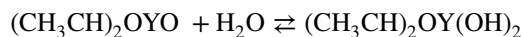
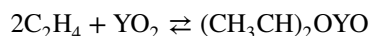
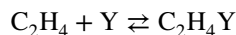
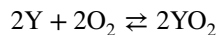
We were not able to fit our experimental results with the model of Rahman et al. [9]. Thus, the model needs modifications for our case since we are using a different catalyst. Parameter estimation results indicate that the main reactions taking place are the oxidation of ethane to ethylene and CO_2 and the oxidation of ethylene to acetic acid. Some of acetic acid is also oxidized to CO and CO_2 . CO is oxidized to CO_2 . The final reaction network takes the form of Fig. 2.

The results indicate that oxidation reactions take place on different sites. Ethane oxidation takes place on one site. Ethylene oxidation in presence of water to acetic acid takes place on another site. CO is oxidized to CO_2 on a third site.

The estimation results indicate that a redox mechanism is more suitable to explain the reactions taking place for the oxidation of ethane to ethylene. Equation (14) for ethane oxidation to ethylene takes the familiar form of redox kinetics. The parameters associated with the oxidation of ethane to ethylene are determined with large t values giving high confidence in their values. For the oxidation of ethane to ethylene, our results agree with Linke et al. [7]. For the oxidation of ethylene to acetic acid our results also agree with that of Linke et al. [7] that acetic acid is related to the formation of a hydroxyl group from water on the active site. There are some controversy of whether ethane or ethylene oxidizes to CO and CO_2 . Burch and Swanakar [12] suggested that CO and CO_2 are formed to a large extent from ethane. On the contrary Thorsteinson et al. [1] suggested that ethylene oxidizes into CO and CO_2 . Our results suggest that CO_2 is mainly obtained from ethane and acetic acid whereas CO is obtained from acetic acid. This CO is then oxidized to CO_2 on sites containing Pd. For reactions involving ethylene, acetic acid and CO a LH kinetic model is suggested.

For the oxidation of ethylene to acetic acid, Rahman et al. [9] suggested two routes one involves water and the second does not involve water. We found that acetic acid formation

from the second route is not significant. The first route involving water needs modification. Let Y be a catalytic center for ethylene oxidation to acetic acid. Consider the following scheme;

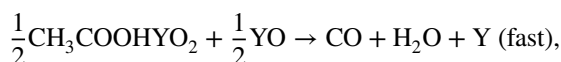
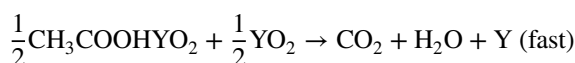
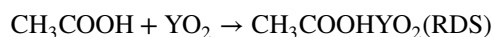
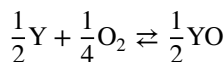
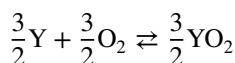


This leads to the following rate equation

$$r_7 = k \frac{k_7 \times P_{C_2H_4}^2 \times P_{O_2} \times P_{H_2O}}{1 + k(P_{O_2} + K_3 \times P_{C_2H_4} + \text{negligible adsorption terms } \dots)}$$

For large k this equation simplifies to Eq. (20).

For the oxidation of acetic acid to CO and CO_2 , we suggest the following scheme



which leads to the following rate equations

$$r_8 = k \frac{k_8 \times P_{CH_3COOH} \times P_{O_2}}{1 + k(P_{O_2} + K_3 \times P_{C_2H_4} + \text{negligible adsorption terms } \dots)}$$

$$r_9 = k \frac{k_9 \times P_{CH_3COOH} \times P_{O_2}}{1 + k(P_{O_2} + K_3 \times P_{C_2H_4} + \text{negligible adsorption terms } \dots)}$$

For large k , these two equations can be approximated by Eqs. (21) and (22).

For the oxidation of CO to CO_2 this occurs through adsorbed oxygen and adsorbed CO on a site denoted by Z such that

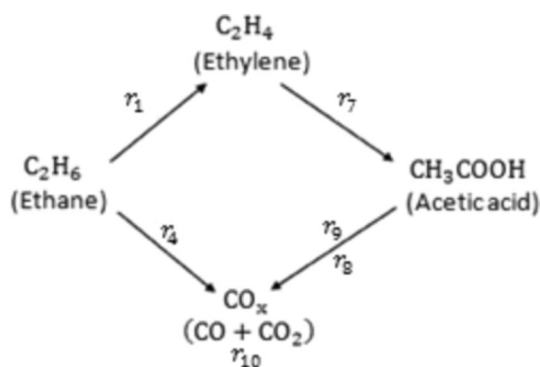
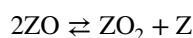
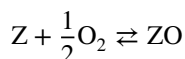
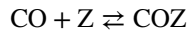
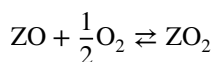


Fig. 2 Modified scheme for ethane partial oxidation



$$r_{10} = k \times k \frac{k_{10} \times P_{\text{CO}} \times P_{\text{O}_2}}{(1 + k(P_{\text{CO}} + K_4 P_{\text{O}_2}))^2}$$

For large k this equation can be approximated by Eq. (23). The order of magnitude of the activation energies is similar to the values reported in the literature [1, 8, 9]. Large activation energy means that the reaction is favored at high temperature. Thus, it is noticed from the values of activation energy and from experimental results that higher temperature favors the formation of CO_2 from oxidation of ethane.

Figures 3, 4 and 5 show the goodness of fit between the observed ethane conversion, CO_2 yield and acetic acid yield and that calculated from the kinetic model. Reasonable fit is obtained for high conversion which would be of practical importance. For low conversion, the fit is slightly distorted possibly because inaccuracy in the experimental results.

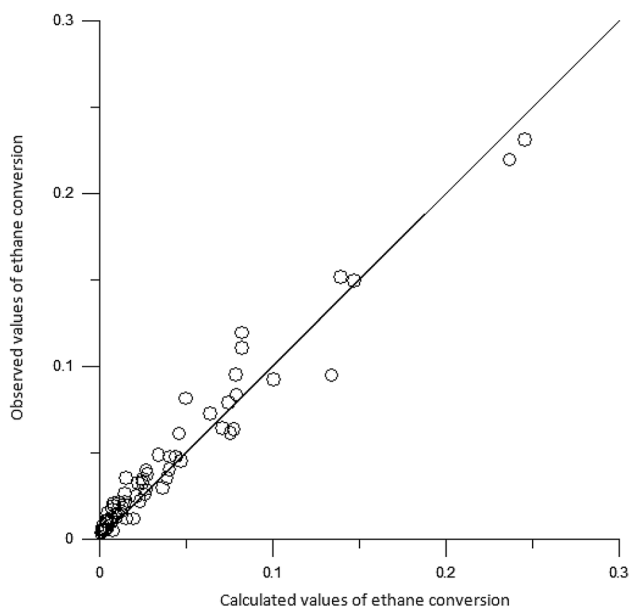


Fig. 3 Observed and calculated conversion for ethane partial oxidation

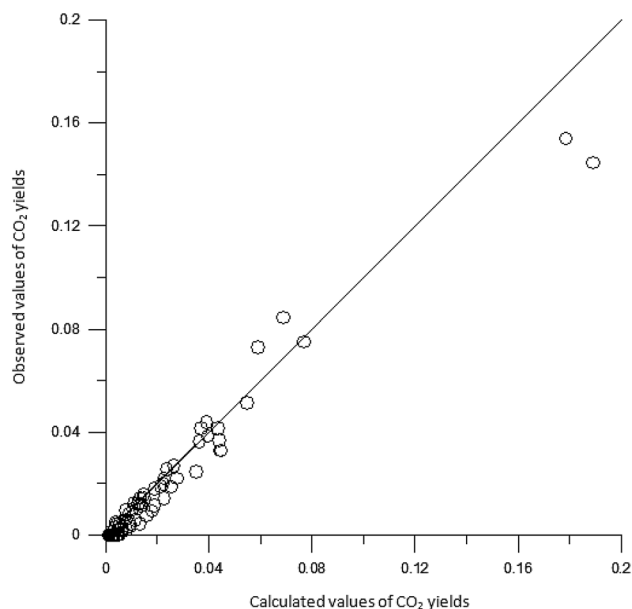


Fig. 4 Observed and calculated yield of CO_2 for partial oxidation of ethane

Conclusion

Our kinetic model has a phenomenological and statistical significance. We assumed a general network, but found through model development and parameter estimation of model parameters that the significant reactions are ethane

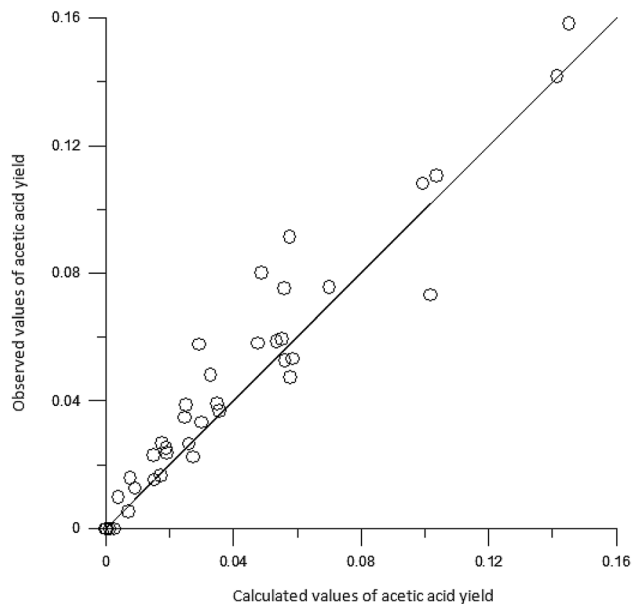


Fig. 5 Observed and calculated values of acetic acid yield for partial oxidation of ethane

oxidation to ethylene and CO_2 , ethylene to acetic acid, CO and CO_2 , and CO to CO_2 . The analysis showed that ethane oxidation to acetic acid and CO is not significant. The reaction takes place on three sites, one for ethane oxidation to ethylene, the second for ethylene oxidation to acetic acid, CO and CO_2 , and the third for the oxidation of CO to CO_2 . In spite of reasonable acetic acid selectivity, there is still scope for catalyst improvement because of the high CO_2 selectivity.

Future work can be directed towards deep understanding of all steps, such as ethylene oxidation, acetic acid oxidation, CO oxidation with these experiments carried out in the presence and absence of water vapor. The species which lead to the partial oxidation products should be identified.

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