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Kinetic Studies of Acetaldehyde Oxidation over Pt/Rh and Pd Monolithic Catalysts in a Spinning-Basket Flow Reactor

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Kinetic studies of acetaldehyde oxidation over Pt/Rh and Pd monolithic automotive catalysts were performed in a spinning-basket flow reactor under atmospheric pressure. The reaction temperature was varied between 350 and 570 K, while the acetaldehyde concentration ranged from 50 to 700 ppm and the oxygen concentration from 2.0 to 10.0% v/v. Among the kinetic models used in the analysis of the experimental data obtained in this work, the one accounting for the surface reaction between adsorbed oxygen and adsorbed reactant was valid for the oxidation over Pt/Rh. As regards the acetaldehyde oxidation over Pd, the kinetic model involving the surface reaction between dissociatively adsorbed reactants was found to yield the most successful fit. According to these models, the activation energy of acetaldehyde oxidation is estimated as 13 150 cal mol⁻¹ over Pt/Rh and 7500 cal mol⁻¹ over Pd catalyst.

Introduction

Ethanol has been suggested as an alternative fuel or as a gasoline additive for car operation. Oxygenated gasolines, including those containing ethanol, form more aldehydes during combustion than non-oxygenated gasolines. Aldehydes such as formaldehyde and acetaldehyde might have an undesirable impact on air quality, because these compounds form photochemically active reactant radicals and toxic peroxyacetyl nitrates. Although the amounts of aldehyde emissions are extremely small, they are of great concern, as emissions standards are going to be more stringent for gasoline vehicles in the future. In California, formaldehyde already belongs to the regulated emissions, and acetaldehyde is one of five candidates on the list for future regulated emissions proposed by the U.S. Environmental Protection Agency.

Some work has been reported on the oxidation of various aldehydes such as formaldehyde¹ and acetaldehyde. Mao and Vannice² studied the oxidation of acetaldehyde in a differential flow reactor under atmospheric pressure over silver dispersed on high-surface-area α -alumina catalysts. The initial concentrations of acetaldehyde and oxygen were 20 and 8% v/v, respectively. The reactor temperature was in the range 483–503 K. Carbon dioxide and methanol as a minor product were detected in the reactor effluent. It was shown that the oxidation occurred on both silver and the support, and cesium addition to the silver strongly enhanced the complete oxidation of acetaldehyde.

McCabe and Mitchell³ studied the catalytic oxidation of acetaldehyde in a laboratory flow reactor over alumina-supported catalysts containing 4 wt % Cu and 2 wt % Cr, 0.1 wt % Pt, and 4 wt % Mn. Carbon dioxide was the principal product, and carbon monoxide was also detected. Pt was found to promote the oxidation at lower temperatures than Cu–Cr and Mn catalysts.

Nagal and Gonzalez⁴ examined the oxidation of acetaldehyde in a fixed-bed flow reactor on silica-supported Pt catalysts. The acetaldehyde concentration was in the range 1100–1400 ppm, and the oxygen concentration was 2000 ppm. In addition to carbon dioxide, acetic acid was also detected in the oxidation products. They suggested that the oxidation of acetaldehyde over Pt/SiO₂ proceeds by a Langmuir–Hinshelwood mechanism in which the rate-determining step is the reaction between chemisorbed oxygen and an adsorbed acetaldehyde species. The activation energies that they measured for carbon dioxide formation on Pt^{Cl}/SiO₂ and Pt^{NH₃}/SiO₂ were 7400 and 10 270 cal mol⁻¹, respectively.

Pettersson et al.⁵ studied the effect of the support material on the oxidation of acetaldehyde with a gas-phase concentration of 100 ppm over Pt and Pd catalysts in the presence of nitric oxide, steam, carbon monoxide, and excess oxygen in a tubular quartz reactor. Acetaldehyde was oxidized to carbon dioxide without any side reactions of importance. The Pt catalysts proved to be more active than the Pd catalysts, especially when titania was used as the support material. Pt on titania and Pd on alumina were the most active catalysts in the interval 350–425 K, compared to CeO₂ and SiO₂ as support materials.

Rajesh and Ozkan⁶ studied the oxidation of acetaldehyde over copper, chromium, and copper–chromium catalysts in a tubular fixed-bed integral reactor with an external recycle loop. The oxidation experiments were performed with a recycle ratio of 50 to simulate CSTR behavior in the reactor. The concentrations of acetaldehyde and oxygen in the reactor feed were 500 and 2500 ppm, respectively. Below 470 K, the Cr catalyst was the most active, whereas above 470 K, the Cu catalyst had the highest activity. Carbon dioxide was the only oxidation product detected.

Zhou and Akgerman⁷ studied the catalytic oxidation of acetaldehyde over a Pt/TiO₂ catalyst in supercritical carbon dioxide in a fixed-bed reactor. The oxidation experiments were conducted in the temperature range 423–548 K at a pressure of 8.96 MPa with an ap-

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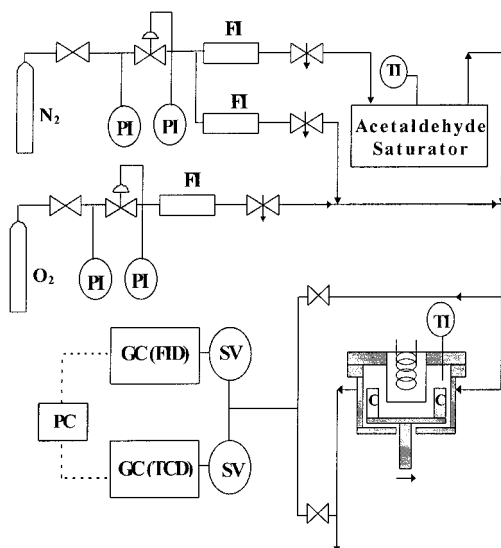


Figure 1. Experimental setup: PI, pressure indicator; FI, flow indicator; TI, temperature indicator; SV, sampling valve; GC, gas chromatograph; C, catalyst.

proximate 4.7:1 molar ratio of oxygen to acetaldehyde in the feed and an inlet acetaldehyde concentration of 1350 ppm. In addition to carbon dioxide, trace amounts of carbon monoxide were generated during acetaldehyde oxidation. They estimated an activation energy of 10 600 cal mol⁻¹ for the oxidation of acetaldehyde to carbon dioxide, assuming that oxygen and acetaldehyde were dissociatively adsorbed on the catalyst surface.

The majority of the above-mentioned studies have been conducted in tubular reactors. Mass-transfer phenomena appearing in this kind of reactor (especially in oxidation reactions) make intrinsic kinetic studies rather uncertain.

In this paper, the reaction kinetics of the catalytic oxidation of acetaldehyde over commercial catalysts are reported. To control external mass-transfer phenomena the experiments were performed in a spinning-basket mixed reactor for various oxygen concentrations. Two monolithic catalysts have been used. The first catalyst (Pt/Rh) is a typical three-way automotive catalyst used for the elimination of exhaust gas pollutants, and the second (Pd) is an oxidative catalyst used for the reduction of hydrocarbon and carbon monoxide emissions. Pd catalyst can be employed for partial substitution of Pt, as it is significantly cheaper.

Experimental Section

Apparatus and Procedure. The experimental apparatus is shown in Figure 1. All experiments were conducted under atmospheric pressure in a spinning-basket mixed reactor. The reactor was operated in the temperature range of 350–570 K. Two pieces of catalyst (thin slices with a front surface area of 4.8 cm² and a depth of 0.4 cm) were placed in the spinning baskets. The total flow rate of the reactants was 1200 cm³ min⁻¹ at 293 K. Acetaldehyde was introduced into the reactor by bubbling a stream of nitrogen through an acetaldehyde saturator. The saturator was thermostated at 235 K. The initial concentration of acetaldehyde was varied from 250 to 800 ppm (mol/mol), and the oxygen initial concentration from 2.0 to 10.0% v/v. The majority of the kinetic experiments were conducted at the maximum

Table 1. Composition of Each Catalyst

catalyst	Pt (g/g _{cat})	Rh (g/g _{cat})	Ce (g/g _{cat})	Pd (g/g _{cat})
PZM 31344	3.27×10^{-3}	0.64×10^{-3}	51.78×10^{-3}	—
PZM 12007	—	—	—	3.60×10^{-3}

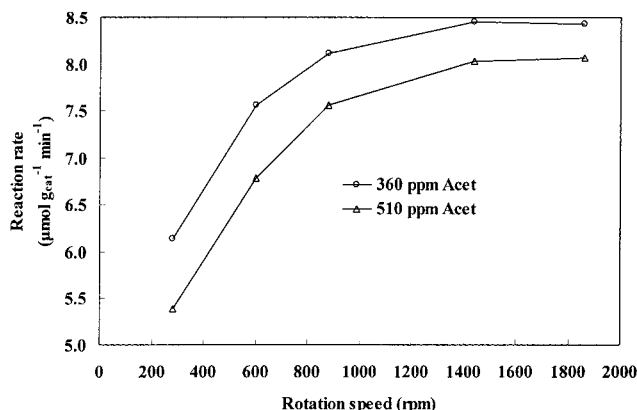


Figure 2. Reaction rates of acetaldehyde oxidation at 478 K in excess oxygen (3.7% v/v) over Pt/Rh for various catalyst rotation speeds.

speed of 1860 rpm of the spinning baskets, where the external mass-transfer phenomena were found to be negligible.

Catalysts. Two commercial catalysts supplied by Allied Signal Co. were used. The catalyst load in the reactor was 1.7075 g for the Pt/Rh type and 1.6402 g for Pd type. The catalytic support consisted of ceramic monolith made of cordierite and a substrate of γ -Al₂O₃. The density of the monolith was 400 square cells per square inch. The composition of each catalyst is shown in Table 1. The catalysts were heated at 543 K in hydrogen for 2 h prior to the oxidation experiments to provide a clean catalyst surface.

Analysis. The reactor feed and product gases were analyzed by two online gas chromatographs via two eight-port valves. The first gas chromatograph was equipped with a flame ionization detector (FID). A Porapak Q column (50–80 mesh, 10 ft \times 1/8 in.) operated at 170 °C was used for the detection of the organic compounds. The second gas chromatograph was equipped with a thermal conductivity detector (TCD). A molecular sieve column (12 ft, 5 Å, 60–80 mesh) operated at 115 °C was used for the detection of carbon dioxide and oxygen. The detection limit of the FID was 5 ppm, and that of the TCD was 150 ppm. The acceptable error in the steady-state carbon balance was $\pm 7\%$. The signals from the detectors were processed by a computer via analog-to-digital converters. Unburned acetaldehyde, carbon dioxide, and small amounts of methane were present in the reactor effluent, whereas diethyl ether, ethylene, acetic acid, and carbon monoxide were not detected.

Results and Discussions

External Mass-Transfer Phenomena. Acetaldehyde oxidation was examined at various catalyst rotation speeds in order to investigate the appropriate experimental conditions that would ensure the elimination of external mass-transfer phenomena. The results showed that the reaction rates of acetaldehyde catalytic oxidation are almost constant at a catalyst rotation speed of greater than 1400 rpm. The results from a

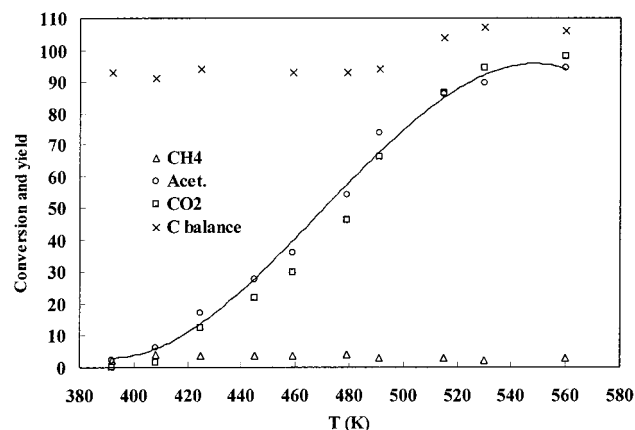


Figure 3. Conversion, carbon balance, and product yield during oxidation of acetaldehyde (450 ppm) in excess oxygen (3.7% v/v) over Pt/Rh.

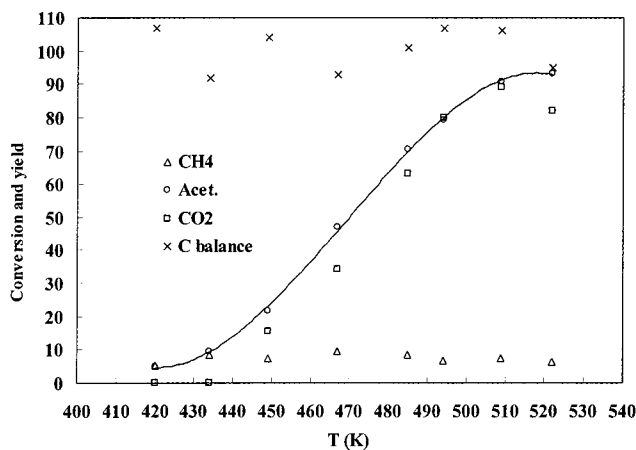


Figure 4. Conversion, carbon balance, and product yield during oxidation of acetaldehyde (522 ppm) in excess oxygen (3.7% v/v) over Pd.

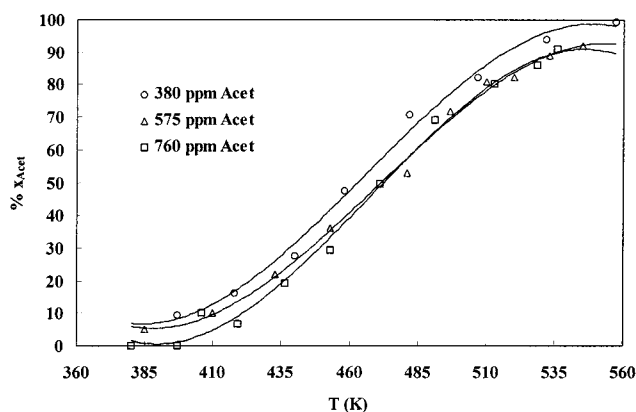


Figure 5. Effect of acetaldehyde concentration on its conversion in the presence of 9.2% v/v oxygen over Pt/Rh.

typical experimental run are presented in Figure 2 as the calculated reaction rate versus rotation speed for a constant temperature and reactant feed rate. These results confirm the strong influence of external mass-transfer phenomena on the reaction rate.

Conversion and Product Yields. Carbon dioxide and small amounts of methane were the only products detected from acetaldehyde oxidation over the catalysts tested (Figures 3 and 4). Because the system is about 90–99% N_2 , it is reasonable to assume a constant overall density of the system at constant temperature and pressure. Thus, the conversion of acetaldehyde,

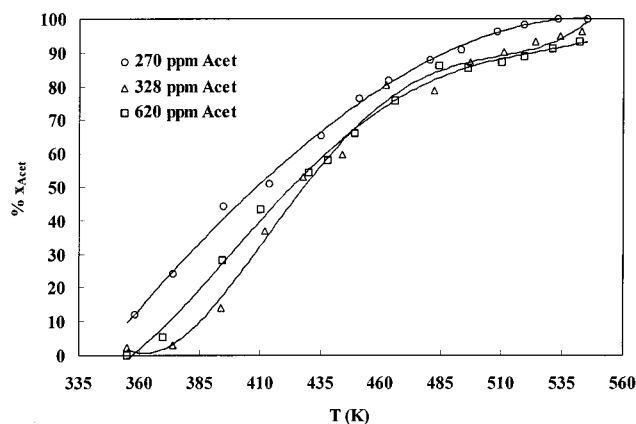


Figure 6. Effect of acetaldehyde concentration on its conversion in the presence of 9.2% v/v oxygen over Pd.

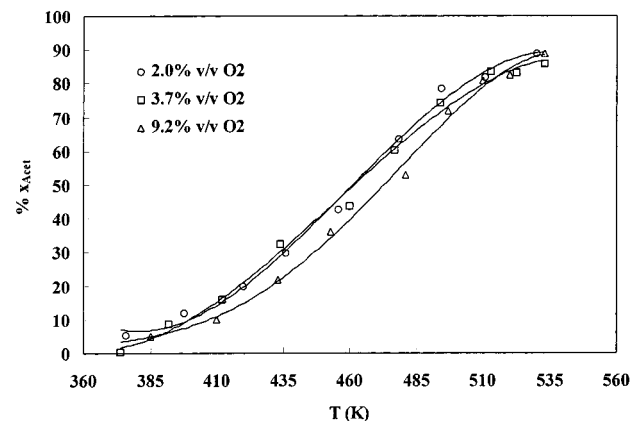


Figure 7. Effect of oxygen concentration on the conversion of acetaldehyde over Pt/Rh.

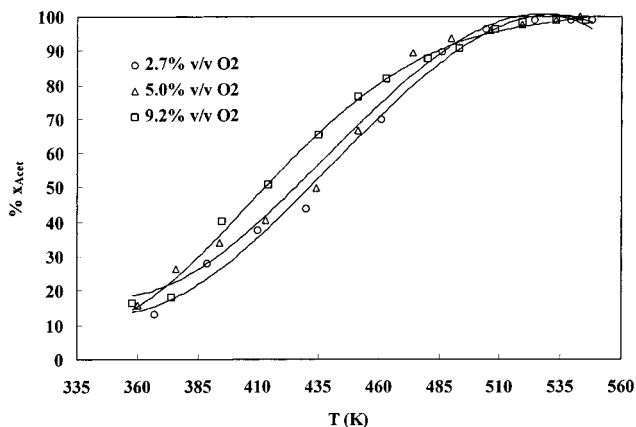


Figure 8. Effect of oxygen concentration on the conversion of acetaldehyde over Pd.

x_{Acet} , and the yields of carbon dioxide and methane, y_{CO_2} and y_{CH_4} , respectively, can be calculated from the following definitions:

$$x_{Acet} = (C_{Acet}^0 - C_{Acet})/C_{Acet}^0 \times 100\%$$

$$y_{CO_2} = C_{CO_2}/2C_{Acet}^0 \times 100\%$$

$$y_{CH_4} = C_{CH_4}/2C_{Acet}^0 \times 100\%$$

The carbon balance F is defined as

$$F = (F_{CO_2} + F_{CH_4} + 2F_{Acet})/2F_{Acet}^0 \times 100$$

Table 2. Estimation of Various Models Parameters

model	rate-limiting step	rate expression	k_R ($\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$)	K_{O_2} ($\text{cm}^3 \mu\text{mol}^{-1}$)	K_{Acet} ($\text{cm}^3 \mu\text{mol}^{-1}$)	MRSS
1. Pt/Rh	surface reaction between adsorbed oxygen and adsorbed reactant	$\frac{k_R k_{O_2} k_{\text{Acet}} C_{O_2} C_{\text{Acet}}}{(1 + k_{O_2} C_{O_2} + k_{\text{Acet}} C_{\text{Acet}})^2}$	$k_0 = 3.14 \times 10^8$ $E = 13157 \text{ cal mol}^{-1}$	$k_0 = 0.38$ $E = 2000 \text{ cal mol}^{-1}$	$k_0 = 43.82$ $E = 110 \text{ cal mol}^{-1}$	0.77 2.08
1. Pd			$k_0 = 1.23 \times 10^6$ $E = 8626 \text{ cal mol}^{-1}$	$k_0 = 0.53$ $E = 1795 \text{ cal mol}^{-1}$	$k_0 = 512.45$ $E = 30 \text{ cal mol}^{-1}$	
2. Pt/Rh	surface reaction between dissociatively adsorbed oxygen and reactant	$\frac{k_R (k_{O_2} k_{\text{Acet}} C_{O_2} C_{\text{Acet}})^{1/2}}{[1 + (k_{O_2} C_{O_2})^{1/2} + (k_{\text{Acet}} C_{\text{Acet}})^{1/2}]^2}$	$k_0 = 1.43 \times 10^8$ $E = 11261 \text{ cal mol}^{-1}$	$k_0 = 0.33$ $E = 1990 \text{ cal mol}^{-1}$	$k_0 = 0.04$ $E = 2000 \text{ cal mol}^{-1}$	0.97 0.43
2. Pd			$k_0 = 3.57 \times 10^5$ $E = 7500 \text{ cal mol}^{-1}$	$k_0 = 2.34$ $E = 10 \text{ cal mol}^{-1}$	$E = 2000 \text{ cal mol}^{-1}$	
3. Pt/Rh	surface reaction between adsorbed oxygen and gas-phase reactant	$\frac{k_R k_{O_2} C_{O_2} C_{\text{Acet}}}{1 + k_{O_2} C_{O_2}}$	$k_0 = 1.44 \times 10^{11}$ $E = 17047 \text{ cal mol}^{-1}$	$k_0 = 22.92$ $E = - \text{cal mol}^{-1}$		19.41 15.04
3. Pd			$k_0 = 1.11 \times 10^{11}$ $E = 16566 \text{ cal mol}^{-1}$	$k_0 = 18.36$ $E = - \text{cal mol}^{-1}$		
4. Pt/Rh	Mars-van Krevelen	$\frac{k_R k_{O_2} C_{O_2} C_{\text{Acet}}}{k_{O_2} C_{O_2} + \gamma k_R C_{\text{Acet}}}$	$k_0 = 6.17 \times 10^9$ $E = 14806 \text{ cal mol}^{-1}$	$k_0 = 1.06 \times 10^{13}$ $E = - \text{cal mol}^{-1}$		3.74 16.75
4. Pd	mechanism		$k_0 = 1.54 \times 10^{11}$ $E = 17191 \text{ cal mol}^{-1}$	$k_0 = 9.99 \times 10^{10}$ $E = 1234 \text{ cal/mol}$		
5. Pt/Rh	surface reaction between adsorbed reactant and gas-phase oxygen	$\frac{k_R k_{\text{Acet}} C_{O_2} C_{\text{Acet}}}{1 + k_{\text{Acet}} C_{\text{Acet}}}$	$k_0 = 3.53 \times 10^6$ $E = 12604 \text{ cal mol}^{-1}$		$k_0 = 9.73$ $E = 1870 \text{ cal mol}^{-1}$	58.52 48.77
5. Pd			$k_0 = 6.71 \times 10^{10}$ $E = 12614 \text{ cal mol}^{-1}$		$k_0 = 0.0080$ $E = 486 \text{ cal mol}^{-1}$	

The carbon balance remains near unity for most of the experiments. Carbon dioxide is the main product of acetaldehyde oxidation. Fifty-percent conversions are achieved at 465 K over Pt/Rh and at 445 K over Pd, whereas 90% conversions are observed at 530 and 500 K over Pt/Rh and Pd, respectively. The production of methane is below 10% at all operating conditions of the reactor, and it is almost independent of temperature.

Effect of Acetaldehyde Concentration. The effect of the variation in the acetaldehyde concentration on its oxidation under excess-oxygen conditions was studied. In the case of Pt/Rh, an increase in the acetaldehyde concentration from 380 to 575 ppm inhibits the oxidation (Figure 5). An increase from 575 to 760 ppm has no effect on the oxidation. In the case of Pd, an increase in the acetaldehyde concentration from 270 to 328 ppm has a negative effect on the oxidation, whereas a further increase to 620 ppm does not appear to affect the acetaldehyde conversion (Figure 6).

Variation of Oxygen Concentration. The effect of the oxygen concentration on the acetaldehyde conversion, with all the other feedstream conditions kept constant, was examined. The conversion versus temperature curves obtained in these experiments are presented in Figures 7 and 8. An increase of oxygen concentration from 2.0 to 3.7% has no significant effect, whereas a further increase to 9.2% appears to inhibit the oxidation of acetaldehyde in the range of 410–490 K over the Pt/Rh catalyst. The oxidation of acetaldehyde over Pd is promoted by an increase in the oxygen concentration from 5.0 to 9.2% in the range of 400–470 K.

Discussion

Modeling. Various models have been proposed for the oxidation of volatile organic compounds. Nagal and Gonzalez⁴ suggested that the experimental results from acetaldehyde oxidation indicated a Langmuir–Hinshelwood oxidation mechanism, whereas Chuang et al.⁸ applied the Mars–van Krevelen mechanism to describe the catalytic oxidation of formaldehyde. Zhou and Akgerman⁷ assumed that the oxidation of acetaldehyde in supercritical carbon dioxide proceeded by dissociative adsorption of acetaldehyde and oxygen on the catalyst surface.

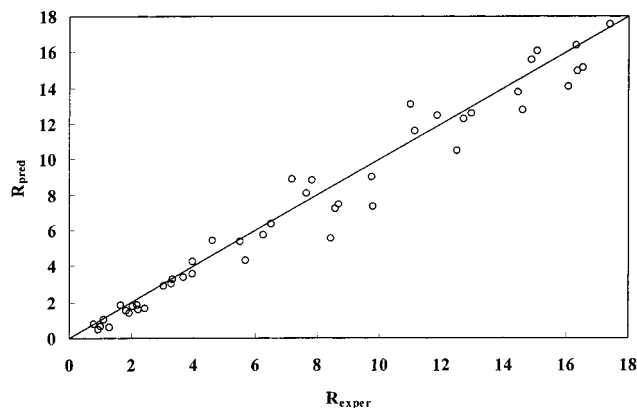


Figure 9. Predicted versus experimental reaction rates of acetaldehyde over Pt/Rh.

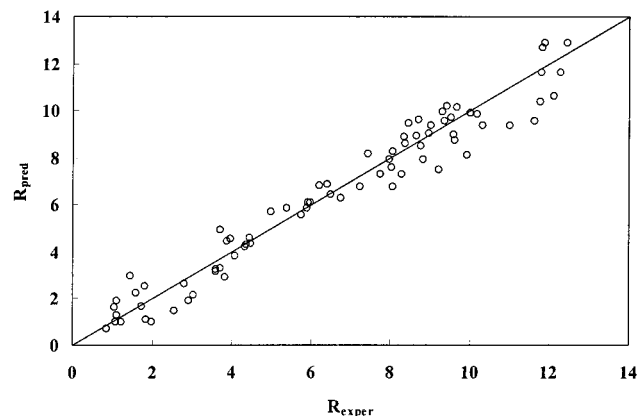


Figure 10. Predicted versus experimental reaction rates of acetaldehyde over Pd.

The mass balance in a basket-type mixed reactor is

$$R = (C_{\text{Acet}}^{\circ} - C_{\text{Acet}})Q/W$$

The Marquardt–Levenberg method was used for the minimization of the objective function for the residual sum of squares

$$\text{RSS} = \sum (R_{\text{pred}} - R_{\text{exper}})^2$$

The mean residual sum of squares

$$\text{MRSS} = \text{RSS}/(N_{\text{obs}} - N_{\text{param}})$$

was used for the comparison of the models, where N_{obs} is the number of experimental observations and N_{param} is the number of model parameters. Only values of experimental rates corresponding to conversions from 15 to 85% were used for the estimation of the kinetic parameters.

Several Langmuir–Hinshelwood models were tested in this study (Table 2). The following rate expressions were ascertained to be superior than the others (Figures 9 and 10):

$$\text{model 1} \quad R = \frac{k_R k_{\text{O}_2} k_{\text{Acet}} C_{\text{O}_2} C_{\text{Acet}}}{(1 + k_{\text{O}_2} C_{\text{O}_2} + k_{\text{Acet}} C_{\text{Acet}})^2}$$

$$\text{model 2} \quad R = \frac{k_R (k_{\text{O}_2} k_{\text{Acet}} C_{\text{O}_2} C_{\text{Acet}})^{1/2}}{[1 + (k_{\text{O}_2} C_{\text{O}_2})^{1/2} + (k_{\text{Acet}} C_{\text{Acet}})^{1/2}]^2}$$

The first model takes into account the surface reaction between adsorbed oxygen and reactant, whereas the second model assumes surface reaction between dissociatively adsorbed oxygen and reactant. The final reaction rate expressions were obtained by the manipulation of the following steps:

(i) Existence of uncovered catalytic surface sites

$$\text{models 1 and 2} \quad \Theta_{\text{Acet}} + \Theta_{\text{O}_2} + \Theta_s = 1$$

(ii) Adsorption (dissociative in the case of the second model) of oxygen and acetaldehyde

$$\text{model 1} \quad k_a^{\text{Acet}} C_{\text{Acet}} \Theta_s = k_d^{\text{Acet}} \Theta_{\text{Acet}}$$

$$k_a^{\text{O}_2} C_{\text{O}_2} \Theta_s = k_d^{\text{O}_2} \Theta_{\text{O}_2}$$

$$\text{model 2} \quad k_a^{\text{Acet}} C_{\text{Acet}} \Theta_s^2 = k_d^{\text{Acet}} \Theta_{\text{Acet}}^2$$

$$k_a^{\text{O}_2} C_{\text{O}_2} \Theta_s^2 = k_d^{\text{O}_2} \Theta_{\text{O}_2}^2$$

From the above, the following expressions are derived:

$$\text{model 1} \quad \Theta_{\text{Acet}} = K_{\text{Acet}} C_{\text{Acet}} / (1 + K_{\text{Acet}} C_{\text{Acet}} + K_{\text{O}_2} C_{\text{O}_2})$$

$$\Theta_{\text{O}_2} = K_{\text{O}_2} C_{\text{O}_2} / (1 + K_{\text{Acet}} C_{\text{Acet}} + K_{\text{O}_2} C_{\text{O}_2})$$

model 2

$$\Theta_{\text{Acet}} = K_{\text{Acet}}^{1/2} C_{\text{Acet}}^{1/2} / (1 + K_{\text{Acet}}^{1/2} C_{\text{Acet}}^{1/2} + K_{\text{O}_2}^{1/2} C_{\text{O}_2}^{1/2})$$

$$\Theta_{\text{O}_2} = K_{\text{O}_2}^{1/2} C_{\text{O}_2}^{1/2} / (1 + K_{\text{Acet}}^{1/2} C_{\text{Acet}}^{1/2} + K_{\text{O}_2}^{1/2} C_{\text{O}_2}^{1/2})$$

where

$$K_{\text{Acet}} = k_a^{\text{Acet}} / k_d^{\text{Acet}}$$

$$K_{\text{O}_2} = k_a^{\text{O}_2} / k_d^{\text{O}_2}$$

(iii) Surface reaction between dissociatively adsorbed oxygen and acetaldehyde

$$R = k_R \Theta_{\text{Acet}} \Theta_{\text{O}_2}$$

In the case of Pt/Rh, both models describe sufficiently the acetaldehyde oxidation, but the first is more accurate. The Mars–van Krevelen mechanism also fits the experimental data to some extent. In the case of Pd, the second model is obviously superior, but the first is also satisfactory. Thus, the activation energy of acetaldehyde oxidation over Pt/Rh is estimated to be 13 150 cal mol⁻¹, and it is estimated to be significantly lower, 7500 cal mol⁻¹, over Pd catalyst.

Conclusions

Carbon dioxide and small amounts of methane are the products of acetaldehyde oxidation over Pt/Rh and Pd monolithic catalysts. For an acetaldehyde concentration range between 50 and 700 ppm and a temperature range between 360 and 560 K, the reaction rate of the oxidation is inhibited by acetaldehyde for both catalysts tested, whereas the oxygen has a negative effect only in the case of the Pt/Rh catalyst. A kinetic model that takes account of the surface reaction between adsorbed oxygen and adsorbed reactant is valid for the oxidation over Pt/Rh catalyst. The oxidation process of acetaldehyde over Pd catalyst was found to be represented by a kinetic model involving the surface reaction between dissociatively adsorbed reactants. According to the above models, the activation energy of acetaldehyde oxidation is estimated as 13 150 cal mol⁻¹ over Pt/Rh and 7500 cal mol⁻¹ over Pd catalysts.

Nomenclature

C_{MTBE}^∞ = initial molar concentration of MTBE, $\mu\text{mol cm}^{-3}$

C_i = molar concentration of the compound i , $\mu\text{mol cm}^{-3}$

E_A = activation energy, cal mol⁻¹

F = carbon balance

F_i = molar flow rate of the compound i , $\mu\text{mol min}^{-1}$

F_{MTBE}^∞ = initial molar flow rate of MTBE, $\mu\text{mol min}^{-1}$

Q = total volume rate of the feed, $\text{cm}^3 \text{min}^{-1}$

ΔH_i = adsorption energy of the compound i , cal mol⁻¹

K_i = adsorption equilibrium constant of the compound i , $\text{cm}^3 \mu\text{mol}^{-1}$

k_R = rate constant of reaction, $\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$

MRSS = mean residual sum of squares

N_{obs} = number of experimental observations

N_{param} = number of model parameters

R = reaction rate, $\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$

R_{exper} = experimental reaction rate, $\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$

R_{pred} = predicted reaction rate, $\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$

RSS = residual sum of squares

W = mass of catalyst, g

x_i = conversion of the compound i

y_i = conversion of the compound i

Greek Symbols

Θ_i = fraction of surface covered by compound i

Θ_s = fraction of free surface

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