

The Influence of Platinum Concentration and Particle Size on the Kinetics of Propane Oxidation over Pt/ γ -Alumina

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For the regulation of automotive emissions it is of interest to understand the parameters that control the oxidation rates of different hydrocarbon species. Propane oxidation was selected as a model reaction for this investigation. Catalysts were prepared by multiple impregnation of γ -alumina with chloroplatinic acid. Concentrations ranged from 0.03 to 30 wt% Pt. The reaction took place in a recirculation batch reactor with an initial mixture of 10 Torr C_3H_8 , 100 Torr O_2 , and 650 Torr Ar. The oxidation rate increased sixfold with increasing Pt concentration. When calculated per Pt surface atom, based on CO chemisorption, the rate increased by two orders of magnitude in the same Pt concentration range. The apparent activation energy remained unchanged at 22.1 kcal/mol within a standard deviation of ± 3.4 kcal/mol. The increase in specific reaction rate with particle size was confirmed by sintering experiments. The rate increase reflects an increase in the preexponential factor. The results suggest that propane oxidation is expedited by a favorable ensemble of active Pt sites, which are more likely to form on larger crystallites. Kinetic parameters of propane and methane oxidation are compared. Theoretical site densities, derived from fundamental kinetics for common reaction mechanisms, are compared with the number of Pt surface atoms as measured by chemisorption. © 1991 Academic Press, Inc.

INTRODUCTION

For the most economical use of Pt in automotive catalysts it is essential to know the relationship between Pt particle size and catalytic activity. In particular, it is of interest to know whether a unique particle size exists which maximizes the catalytic activity of a given amount of Pt. This matter was investigated for the oxidation of hydrocarbons, specifically alkanes. It was shown previously (1, 2) that the notoriously slow oxidation of methane is "structure sensitive" on Pt and is characterized by an optimum particle size (1). Structure sensitivity can originate from several structural attributes, and is, in general, characterized by a change in turnover frequency (TOF), i.e. specific rate per surface atom, with particle size. Alkanes, as a class, are known for their relatively slow oxidation, when compared to other hydrocarbon species, and are therefore of special interest for automotive emission control. Earlier studies from this labo-

ratory (3) indicate that propane oxidation on Pt is also structure sensitive. Thus, it was found that the TOF was larger for Pt wire than for Pt supported on γ -alumina. It was of interest to evaluate this structure sensitivity of propane oxidation more quantitatively and to determine whether a maximum TOF for methane and propane oxidation exists for the same particle size. The reaction mechanisms of methane and propane oxidation are *a priori* different, since methane oxidation proceeds through the scission of C-H bonds, while propane oxidation requires additional scission of C-C bonds.

EXPERIMENTAL

Experimental details concerning the catalysts and the reactor system have been described in a report on the oxidation of methane over Pt/ γ -alumina (1), and therefore are kept brief. The catalyst samples, ranging in concentration from 0.03 to 30 wt% Pt, were taken from the same batch used in the previous investigation. The catalysts were pre-

pared by multiple impregnation of γ -alumina (Degussa, aluminum oxide C) with chloroplatinic acid. Sample pretreatment, after calcination at 600°C, consisted of reduction in hydrogen at 400°C for 2 h, followed by heating in oxygen at 500°C for 20 h, which maximizes Pt dispersion on a given alumina surface (1). The alumina BET surface area after calcination was $85 \pm 5 \text{ m}^2/\text{g}$, as measured by Ar and N_2 adsorption at the temperature of liquid nitrogen.

A recirculation batch reactor (4) was used to measure reaction rates. The volume of the glass apparatus was about 400 cm^3 , excluding the reactor, which had a volume of about 130 cm^3 . To prevent mass-transfer limitations, conditions were chosen such that a minimum time of 2 h was allowed to complete a reaction isotherm. The gas composition was measured as a function of time by injecting small gas samples into a mass spectrometer (VG Quadrupoles). The analysis by mass spectrometer was based on the calibrated parent peaks of O_2 , Ar, and CO_2 at m/e 32, 40, and 44, respectively, and the C_3H_8 fragmentation peak at $m/e = 29$. The concentrations of C_3H_8 , O_2 , and CO_2 were determined from the known amount of Ar and the Ar peak intensity at $m/e = 40$. The propane contribution at $m/e = 44$ was subtracted to obtain the CO_2 peak intensity. The mass balance was based on the disappearance of propane and oxygen on the one hand, and the appearance of carbon dioxide on the other. It was concluded from the mass balance that more than 97% of the carbon in propane was converted to CO_2 .

The initial reactant mixture was composed of 1.5 mol% propane and 15 mol% oxygen with Ar as the carrier gas. In most experiments, the initial pressures were 10 and 100 Torr for propane and oxygen, respectively (1 Torr = 133.3 Pa). Thus, the oxygen concentration was twice the amount needed for the complete oxidation of propane. To study catalyst activity as a function of Pt concentration, each reactor charge was fixed at 4 mg Pt. The Pt dispersion, or fraction of Pt atoms exposed on the surface,

was measured by CO chemisorption at room temperature on freshly reduced samples after thorough evacuation. The adsorption capacity of Pt on these samples was found to be the same for carbon monoxide molecules and oxygen atoms. The ratios $\text{CO}:\text{Pt}$ and $\text{O}:\text{Pt}$ equaled 0.7:1. This ratio is in complete agreement with recent oxygen chemisorption data reported by O'Rear *et al.* (5).

RESULTS AND DISCUSSION

Dependence of Reaction Rate on Pt Concentration and Temperature

Propane oxidation kinetics under the conditions used in this investigation can be adequately described as a first-order reaction with respect to propane. Empirically, with excess oxygen used, the reaction rate was found to be independent of the oxygen pressure. Thus, the propane oxidation rate is expressed by the product of propane concentration c_p and the rate constant k

$$\frac{dc_p}{dt} = -kc_p. \quad (1)$$

The rate constant as a function of absolute temperature T is described by a preexponential factor k_0 and an apparent activation energy E

$$k = k_0 \exp\left(\frac{-E}{RT}\right), \quad (2)$$

where R is the gas constant.

In Fig. 1, the decreasing amount of propane in the batch reactor is plotted as a function of time. The linear dependence of the three isotherms in Fig. 1 illustrates the conformity of the reaction to first-order kinetics with respect to propane. The initial deviation from linearity in the upper curve of Fig. 1 is thought to result from a lack of steady-state conditions, which are established more rapidly at higher temperatures. Integration of Eq. (1), expressed as \log_{10} , yields

$$\log c_p = -k't, \quad (3)$$

where

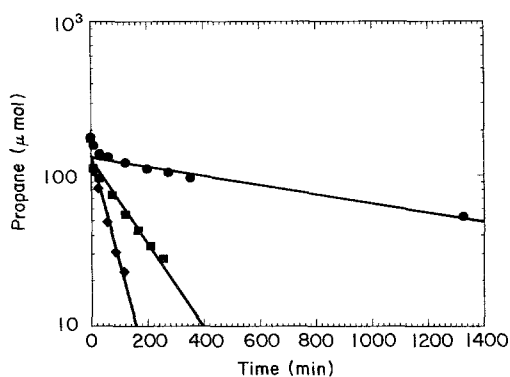


FIG. 1. Reaction isotherms on 0.4 wt% Pt/ γ -alumina at (●) 230°C, (■) 275°C, (◆) 300°C.

$$k' = k \log_{10} e. \quad (4)$$

In a first approach, propane oxidation was studied as a function of Pt concentration to assess Pt activity as a function of Pt particle size. The oxidation rate was measured over a fixed amount of Pt (4 mg), with the total amount of sample varying from 0.01 to 15 g. Rate constants k' at 275°C, derived from the slopes of $\log c_p$ vs t plots, are shown in Fig. 2 as a function of Pt concentration. The open circles represent the k' values obtained on 4 mg Pt. Over the full concentration range, the rate constant k' increases from $1.25 \times 10^{-3} \text{ min}^{-1}$ at 0.03 wt% to $8.04 \times 10^{-3} \text{ min}^{-1}$

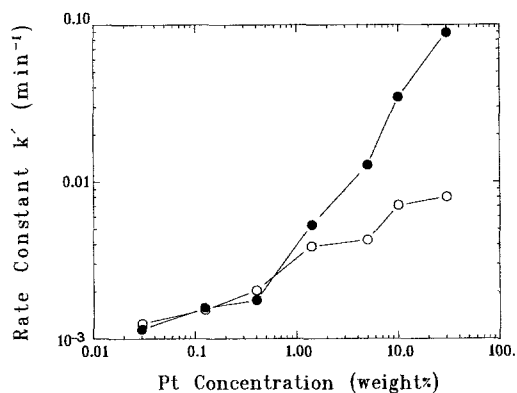


FIG. 2. Rate constant k' as a function of Pt concentration at $T = 275^\circ\text{C}$. Reactor charge is 4 mg Pt for each case. (○) per 4 mg bulk Pt, (●) normalized to surface Pt.

TABLE 1

Pt Dispersion of Catalyst Samples Measured by CO Adsorption, Assuming $\text{CO}_{\text{adsorbed}}/\text{Pt}_{\text{surface atoms}} = 0.70$

| Pt loading (wt%) | Dispersion |
|------------------|------------|
| 0.03 | 1.09 |
| 0.12 | 0.97 |
| 0.40 | 1.15 |
| 1.40 | 0.73 |
| 5.0 | 0.33 |
| 10.0 | 0.20 |
| 30.0 | 0.09 |

at 30 wt% Pt. It is known (6) that at the lower Pt concentrations employed here, the Pt is highly dispersed on the alumina support. As the Pt loading is increased, larger Pt particles are formed with a substantial amount of subsurface Pt atoms. Thus, the increase in k' with Pt concentration over a fixed amount of metal indicates that propane oxidation activity increases considerably with particle size.

The rate increase with particle size can be described more quantitatively by calculating the reaction rate per surface atom. This turnover frequency is derived by dividing the specific rate by the dispersion, i.e., the fraction of Pt surface atoms. The dispersion data were obtained from CO chemisorption measurements (1). Table 1 shows the dispersion as a function of Pt concentration. The results are based on the assumption of a ratio $\text{CO}_{\text{chemisorbed}}:\text{Pt}_{\text{surface atoms}} = 0.7$. The solid circles in Fig. 2 represent k' over 4 mg of Pt after division by the dispersion. The highly dispersed Pt at 0.03 wt% yields a k' value of $1.15 \times 10^{-3} \text{ min}^{-1}$, which increases by a factor of 80 as the Pt concentration is increased to 30 wt%. Thus, as expected, the increase in activity with particle size is much more pronounced after correcting for inaccessible subsurface Pt.

The dependence on particle size can be seen more directly in Fig. 3. Here, the rate constant, based on TOF, is plotted as a function of Pt dispersion and the increase with particle size is quite obvious. Two disper-

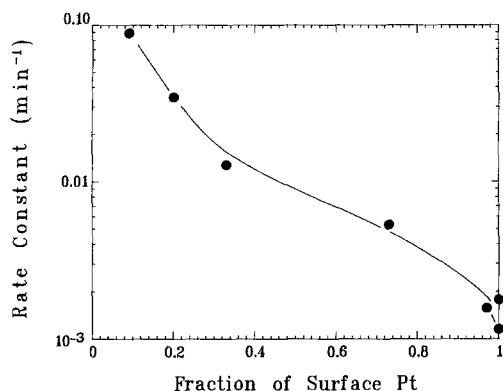


FIG. 3. Rate constant at $T = 275^\circ\text{C}$, normalized to surface Pt, as a function of Pt dispersion.

sion values in Table 1 exceeding 1.0 are plotted in Fig. 3 at the limiting dispersion of 1.0.

The apparent activation energy as a function of concentration is plotted in Fig. 4. The activation energy remains constant at 22.1 ± 3.4 kcal/mol. A least-squares fit of the energy values yields a linear relationship described by an ordinate intercept of 22.1 and a slope of 0.20. A low correlation coefficient of 0.27 indicates that any systematic change in the activation energy with concentration is overwhelmed by data scatter. The derived average value is in agreement with literature data. Reported activation energies for propane oxidation range from 17.0 (7–9) to 25.0 kcal/mol (3).

The Arrhenius equation (Eq. (2)) describes the rate constant by two parameters k_0 and E . Since the results indicate that E remains constant, the substantial change in k with Pt concentration is associated with an increase of the preexponential factor. Based on transition state theory, reaction rates can be related to the density of the catalytically active sites associated with the slow step of the reaction. Reaction rates of the basic reaction mechanisms are invariably proportional to the density of those active sites, or site ensembles, which control the reaction (10, 11). Thus, the data in Fig. 2 indicate that the fraction of site ensembles favorable for propane oxidation increases by two or-

ders of magnitude as the Pt concentration changes from 0.03 to 30 wt%.

Effects of Pt Sintering and Redispersal on Propane Oxidation Rates

Transmission electron micrographs of Pt/ γ -alumina have shown that the Pt particle size can be increased by sintering in hydrogen (6, 12) above 500°C , as well as by raising the Pt concentration. On the other hand, Pt, as prepared in this study, can be redispersed, within certain limits, by exposure to oxygen at 500°C (1, 6, 12–16). If the reaction rate increases with particle size, then it should be possible to take a sample at low Pt loading, where the Pt is highly dispersed, and increase the propane oxidation rate by sintering. A series of sintering experiments substantiated this concept. It was not possible to express the results in terms of TOF, since chemisorption experiments *in situ* could not be performed. Thus, the rate measured over 4 mg Pt is a lower limit of the TOF because the sintering superimposes two effects. As the particles grow in size, the specific activity per surface atom increases, but at the same time, a fraction of surface atoms becomes inactive by moving into the bulk. These experiments were carried out with a sample containing 0.12 wt% of highly dispersed Pt (cf. Table 1). The results of the sintering experiments are summarized in

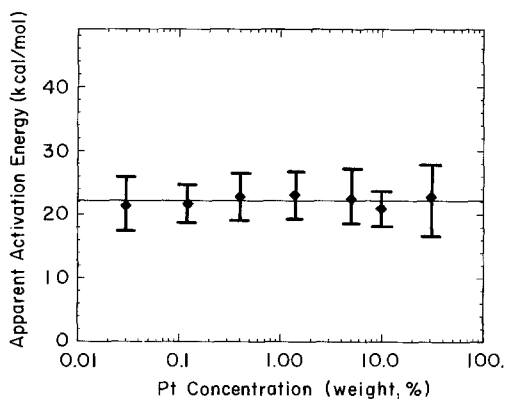


FIG. 4. Activation energy as a function of Pt concentration. The error bars represent standard deviations.

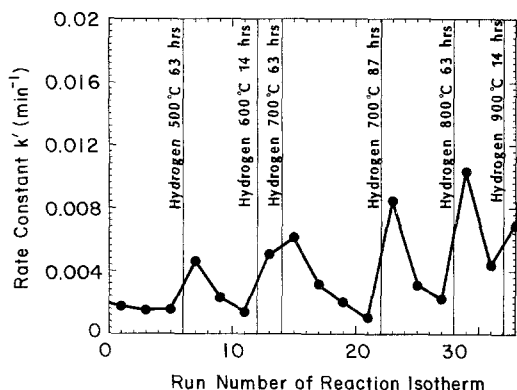


FIG. 5. Changes in rate constant k' at 275°C (per 4 mg bulk Pt) caused by hydrogen pretreatments at different temperatures and exposure times on 0.12 wt% Pt/ γ -alumina.

Fig. 5. The graph shows the rate constant k' , derived from rate measurements at 275°C, after various thermal excursions. The k' values of the initial isotherms (1, 3, and 5) illustrate the reproducibility of the measurements after the standard oxygen treatment at 500°C, yielding a rate constant of $1.5 \times 10^{-3} \text{ min}^{-1}$. After sample exposure to hydrogen at 500°C for 63 h, the rate constant increased substantially to 4.6×10^{-3} (isotherm 7). As expected for sintering, the magnitude of the rate change depends on the temperature and time of exposure. As the sintering temperature was increased stepwise to 800°C, a maximum rate constant of $10.3 \times 10^{-3} \text{ min}^{-1}$ was measured (reaction isotherm 31), which is a sevenfold increase over the initial value. A further increase in temperature to 900°C resulted in a lower rate. At this point the sintering experiments were discontinued. Excessive sintering ultimately defeats the benefits of an increased TOF, as the fraction of surface Pt becomes too small. When the Pt particles increase sufficiently in size, one expects the TOF to remain at a constant value, and thus, the reaction rate over a fixed mass of Pt to decrease. The maximum rate increase obtained in the sintering experiments is comparable to that achieved in the concentration

series (Fig. 2), where the particle size was controlled more systematically.

Sequential propane oxidation isotherms, following the reactivity increase after sintering, show a gradual decrease in k' . For example, the reaction isotherms 17, 19, 21, measured between hydrogen treatments, show a slow return to the rate constant measured in the initial runs. The decrease is too slow to be explained by poisoning of the metal surface by oxygen. The effect is rather attributed to Pt redispersion during the reaction. In the absence of propane, a temperature of at least 450°C is needed to achieve Pt redispersion through oxygen exposure. In the presence of propane, redispersion appears to take place at considerably lower temperatures. Restructuring of catalyst particles, varying with the gas environment, has been reported repeatedly in the literature (17, 18). Indeed, it has been shown recently that Pt restructuring, for example by CO adsorption (19, 20) can take place even at room temperature.

Comparison of Propane and Methane Oxidation Kinetics and Theoretical Considerations

One objective of this study was to explore the possible existence of a unique particle size which yields a maximum alkane-oxidation rate for a given amount of Pt. *A priori*, one would expect the particle size dependence to be different for methane and propane, since methane oxidation proceeds through the scission of C–H bonds, whereas propane requires the scission of C–C bonds. The most conspicuous difference in the kinetics is a change in the apparent activation energy with Pt concentration found for methane oxidation (1) but not for propane oxidation. Furthermore, the particle size of maximum TOF exists at a much smaller Pt concentration, and thus smaller particle size, for the oxidation of methane (5 wt%) than for the oxidation of propane (≥ 30 wt%). The TOF changes with Pt concentration by one order of magnitude for methane, by two orders for propane oxidation.

To discuss the differences between methane and propane oxidation kinetics in more detail, it should be pointed out that platinum supported on γ -alumina exists as two distinct entities (1, 6). At low Pt concentrations, a highly dispersed Pt species dominates. When oxidized, these very small Pt particles require a temperature of about 300°C to be reduced by hydrogen (6). Larger oxidized Pt particles, which exist at higher Pt concentrations and resemble Pt black, can be reduced below 150°C. Thus, reduction at 150°C can be used to discriminate between the two Pt species. Additional information about the structural differences have been obtained by transmission electron microscopy (12), X-ray photoelectron spectroscopy (21), and Raman spectroscopy (22).

The apparent activation energy of methane oxidation changes with Pt concentration (1). Thus, an activation energy of 35.2 ± 1.6 kcal/mol was measured on highly dispersed Pt (0.03–1.4 wt%), a distinctly lower value of 27.4 ± 1.0 kcal/mol on larger particles (≥ 5.0 wt%). In contrast, the value for propane oxidation remained constant at 22.1 ± 3.4 kcal/mol over the same concentration range. It is tempting to associate the observed energy change for methane oxidation with the difference in reduction temperature for dispersed and particulate Pt species. Based on the measured reaction kinetics and a theoretical site density it was speculated that the slow step of methane oxidation is associated with the dissociation of an adsorbed methane molecule or methane–oxygen complex (1). The propane-oxidation data indicate that the energy associated with the slow reaction step remains fixed. The result suggests that either the removal of oxygen from platinum does not affect the activation energy, or that propane oxidation cannot take place on highly dispersed Pt. The latter supposition implies that even at the lowest Pt concentration, there exist some, however few, larger Pt particles among the vast majority of highly dispersed

Pt entities. It is interesting to note that the apparent activation energies of propane oxidation and of methane oxidation on larger Pt particles are comparable. In fact, a closer examination of the error limits (cf. the last four energy values in Table 2 of Ref. (1)) leaves the possibility open that the activation energies are identical.

Another possibility is to associate the activation energy with the breaking of C–H bonds. A value of 18.2 kcal/mol has been deduced from the exchange of hydrogen for deuterium in propane over 5% Pt on pumice (23, 24). Within the experimental error, this value is in agreement with the apparent activation energy measured in this investigation for the oxidation of propane. For methane the energy value for the hydrogen–deuterium exchange is greater by at least 6 kcal/mol.

Calculations of theoretical reaction-site densities provide additional clues to resolve the rate-determining step. As pointed out by Maatman (10, 11) the strength of this method is in the rejection of a proposed reaction mechanism because of a large discrepancy between calculated and measured site density. For example, if the calculation is executed for an Eley–Rideal mechanism with propane molecules from the gas phase reacting with surface oxygen, a total of 1.6×10^{25} reaction sites is calculated for the experimental conditions used here. In reality, a maximum dispersion of the 4 mg of Pt provides only 1.2×10^{19} sites, lower by 6 orders of magnitude than the calculated value, indicating that the Eley–Rideal reaction mechanism is highly unlikely. The numerical basis of these calculations is given in the appendix of this report. Two other plausible reactions governing the propane oxidation are a rapid adsorption of propane followed by a slow dissociation step and a Langmuir–Hinshelwood reaction mechanism. The calculated site densities are listed in Table 2. Slow propane dissociation yields 1.6×10^{18} sites at a Pt concentration of 0.03 wt%, where each Pt atom is considered to

TABLE 2
Calculated Numbers of Reaction Sites per 4 mg
Bulk Pt

| Reaction mechanism (10) | Propane oxidation 0.03 wt% Pt | Methane oxidation | |
|-----------------------------|----------------------------------|----------------------|----------------------|
| | | 0.03–1.4 wt% Pt | 10 wt% Pt |
| Eley–Rideal | 1.6×10^{25} | 9.1×10^{25} | 5.7×10^{23} |
| Slow alkane dissociation | 1.6×10^{18} | 8.6×10^{19} | 5.3×10^{17} |
| Slow oxygen dissociation | 2.8×10^{17} | — | — |
| Langmuir– Hinshelwood | 0.97×10^{15} | 2.1×10^{16} | 0.9×10^{15} |
| Measured site density | 1.2×10^{19} | 1.2×10^{19} | 2.4×10^{18} |

be a surface atom. At this Pt concentration the site density appears to be reasonable when compared to the upper limit of 1.2×10^{19} Pt atoms. However, since the TOF increases almost 100 times as the concentration is increased to 30 wt% Pt, the calculated site density becomes too large by at least a factor of 10. If the dissociation requires multiple adsorption sites, the site density for this mechanism should be smaller by at least one or two orders of magnitude, but never greater than the measured site density (10). It is interesting to note that a somewhat better numerical agreement is found (2.8×10^{17}) if it is assumed that the slow dissociation step is associated with the oxygen molecule. Such a mechanism can be refuted for a different reason, as the reaction rate does not increase with oxygen pressure.

The last case considered here is a Langmuir–Hinshelwood reaction mechanism where oxygen adsorbs strongly enough to cover almost all of the surface (case 3c in Ref. (10)). The site density calculation yields 0.97×10^{15} sites consistent with the experimental site density, which remains lower by at least one order of magnitude, even after an increase in TOF by two orders of magnitude as the Pt concentration is increased to 30 wt%. From these considerations it follows that the most likely mechanism is given by a Langmuir–Hinshelwood expression, where the propane is sparsely

adsorbed on suitable sites or site ensembles.

Propane adsorption on multiple Pt sites would explain the steep increase in the oxidation rate with Pt particle size. It has been pointed out (23) that some reactions take place preferentially on site ensembles predominating on larger crystallites. This type of structure sensitivity can have a pronounced effect on the TOF and the selectivity of a reaction. Propane adsorption is generally pictured by the adsorption of one or more carbon atoms, after hydrogen dissociation, where each carbon atom is attached to one or more adsorption sites (24–27). This is only one plausible explanation *ad hoc*; there are obviously other interpretations possible. Without further experimental evidence an explanation of the observed structure sensitivity remains speculative. The explanation, however, is attractive, as it is based on geometrical considerations and does not require the assumption of a change in activation energy.

In view of these considerations it appears timely to revisit earlier speculations on the oxidation of methane over the same Pt samples (1). It was concluded that methane oxidation on higher concentrations of Pt is consistent with a slow dissociation step, characterized by 5.3×10^{17} sites (cf. Table 2). For the highly dispersed Pt, the same mechanism yields too many sites (8.6×10^{19}). When the calculation of active sites is based on the same Langmuir–Hinshelwood reaction mechanism proposed for the propane oxidation, the number of sites are calculated to be 2.1×10^{16} and 0.9×10^{15} for the highly dispersed Pt and the 10 wt% samples, respectively. The corresponding fraction of active sites to Pt surface atoms are therefore $2.1 \times 10^{16}/1.2 \times 10^{19} = 1.8 \times 10^{-3}$ and $0.9 \times 10^{15}/(0.2 \times 1.2 \cdot 10^{19}) = 3.8 \times 10^{-4}$. At first glance, a decrease by a factor of 4.7 in the fraction of active sites with increasing particle size appears to be questionable; however, within the claimed error limits the fraction of active sites for fully dispersed Pt could be as low as $6.0 \times$

10^{-4} , for larger Pt particles as high as 1.1×10^{-3} . Thus, within the uncertainty of a standard deviation in the apparent activation energies the reaction site density may actually increase with particle size.

Under these considerations the oxidation of methane and propane can essentially be described by the same type of rate-limiting step, which involves a surface reaction of an alkane-oxygen complex. The surface-complex concentration is relatively small, and increases rapidly with particle size for propane. There is no need to invoke the scission of C-C bonds as a rate-limiting step in the oxidation of propane. A surface reaction described by a methane-oxygen complex has also been deduced for Pd film (28). The conclusion was based on a comparison of reaction isotherm shapes for different reaction mechanisms and a quantitative statistical interpretation.

The relatively small number of active sites compared to the total number of Pt surface atoms is consistent with chemisorption data (29). Thus, methane and propane chemisorption measured on Pt films by surface potential changes in a capacitor, albeit executed under reducing conditions at lower temperatures and pressures, indicated alkane adsorption on less than 0.1% of the Pt surface. The Pt film, which is representative for large Pt crystals, was found to chemisorb about twice as much propane as compared to methane. Measurements of methane and propane adsorption on the supported catalysts in this laboratory also implied a very sparse coverage of Pt by these alkanes (30).

CONCLUSIONS

(1) Oxidation of propane on Pt/ γ -alumina is a structure-sensitive reaction manifested by a rate increase with Pt particle size. The particle size depends on Pt concentration and on thermal treatment (sintering and redispersion).

(2) The apparent activation energy of propane oxidation remains constant at 22.1 ± 3.4 kcal/mol. The rate change therefore reflects a change in reaction-site density.

(3) A theoretical reaction-site density calculated for a Langmuir-Hinshelwood reaction mechanism is consistent with the empirical amount of surface Pt. The data suggest that surface oxygen facilitates dissociation of propane molecules.

(4) The effects of structure sensitivity of propane and methane oxidation on Pt/ γ -alumina are quantitatively different. For propane, the change with particle size is more pronounced, and the Pt particle size that defines the maximum TOF is larger. Both reactions are consistent with a slow step in accordance with a Langmuir-Hinshelwood reaction mechanism, characterized by a very low coverage of the catalyst by an alkane-oxygen reaction complex.

APPENDIX: SITE-DENSITY CALCULATIONS (10, 11)

(1) Eley-Rideal

$$L = \frac{vF_{tr}F_{rot} \exp\left(\frac{E}{RT}\right)}{c_g \frac{kT}{h}} \quad (5)$$

(2) Slow Dissociation

$$c_s = v \frac{h}{kT} \sqrt{\frac{F_{tr}F_{rot}}{c_g}} \exp\left(\frac{E}{RT}\right) \quad (6)$$

(3) Langmuir-Hinshelwood

$$L = \frac{2v}{s} \frac{h}{kT} \frac{c'_g F_{tr} F_{rot}}{c_g F'_{tr} F'_{rot}} \exp\left(\frac{E'}{RT}\right) \quad (7)$$

The notations are those listed by Maatman (10). Specific data used for the calculations are: reaction rate $v = 2.58 \times 10^{15}$ (molecules s^{-1} per sample); $T = 548$ K, 0.03 wt% Pt, 1.2×10^{19} Pt surface sites; propane concentration $c_g = 0.524 \times 10^{-6}$ mol/cm³; $c_g = c_p$; oxygen concentration $c'_g = 5.24 \times 10^{-6}$ mol/cm³; activation energy E' , $E = 22.1$ kcal/mol; moment of inertia: propane: $I_A = 28.75 \times 10^{-40}$, $I_B = 99.4 \times 10^{-40}$, $I_C = 112.6 \times 10^{-40}$ g · cm² and oxygen: $I = 19.1 \times 10^{-40}$ g · cm².

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