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Effects of Support Material and Sulfation on Propane Oxidation Activity over Platinum

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Propane oxidation is used as a model reaction to study effects of platinum concentration, support material, and catalyst sulfation. Support materials examined are γ-alumina, zirconia, and silica in a platinum dispersion range from about 0.05 to 1.0. Experiments are conducted with recirculation batch and integral flow reactors. For highly dispersed platinum, the activity decreases in the order zirconia > silica > γ-alumina. Over larger platinum particles, the batch experiments show the same turnover rate on the three supports. On highly dispersed platinum, sulfation, via SO_2 oxidation or H_2SO_4 exposure, significantly increases the catalytic activity of Pt/γ-alumina, while Pt/silica and Pt/zirconia remain unaffected. Surface acid strength is measured with Hammett indicators. Upon sulfation, the acid strength of zirconia and γ-alumina increases, while no change is observed for silica. Acid strength does not have a major influence on propane-oxidation activity. Within the experimental error, the apparent activation energy for propane oxidation is independent of metal concentration, support material, and sulfation, suggesting that changes in activity are primarily the result of a change in reaction-site density.

INTRODUCTION

Sulfur dioxide is a common component in engine exhaust at a typical level of 20 ppm, derived from gasoline and engine oil. Even at such a low concentration, the sulfur can have a variety of effects, both beneficial and detrimental, on the performance of catalytic converters installed in automobiles to lower pollutants. In fact, the presence of SO_2 deters the use of base-metal catalysts known to be readily poisoned by sulfur (*1*). On the other hand, small concentrations of lead from fuel can be prevented from deactivating metals of the Pt group by reacting with SO_2, which under oxidizing conditions forms chemically inert lead sulfate. However, larger deposits of lead sulfate can physically block access to catalytic sites. Other examples are the suppression of alkene and carbon monoxide oxidation over Pt/γ-alumina in the presence of SO_2 (*2, 3*). Conversely, on the same catalyst, propane oxidation is greatly and permanently enhanced by aluminum sulfate, derived from the oxidation of SO_2 (*4*). The favored oxidation of alkanes over alkenes is a beneficial effect, since normally alkanes of short-chain length are oxidized more slowly than their alkene counterparts (*5*). The reason for the observed increase in alkane reactivity caused by SO_2 remains unclear. It has been proposed, however, that new catalytic sites, active for propane oxidation, are generated by the sulfate deposit (*6*).

The objective of this study is to probe further the influence of support and metal structure modifications. For example, a logical question is whether the increase in the activity of small platinum clusters observed when replacing γ-alumina by a zirconia support (*7*) can be further enhanced by sulfating. In particular, it is of interest to compare the effects of sulfation on the activity of platinum on three dissimilar supports, γ-alumina, zirconia, and silica, and to evaluate the influence of surface acid strength introduced by sulfation (*8, 9*).

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EXPERIMENTAL

Catalysts

The Pt/silica series consisted of samples containing 0.10, 0.50, and 4.76 wt% Pt. The catalysts of lower metal loading, 0.10 and 0.50 wt%, were prepared by an ion-exchange method to achieve higher metal dispersion (*10*). Silica, adjusted to pH 10 with aqueous ammonia, was slurried with the desired amount of tetraammine platinum (II) chloride. The mixture was stirred at room temperature for 2 h maintaining the pH at 10. The catalysts were then washed with distilled water, dried overnight at room temperature, and finally dried at 120°C in air for 2 h. The 4.76 wt% Pt/silica catalyst was prepared by multiple impregnation of silica with the desired amount of chloroplatinic acid and then dried in air at 120°C for 2 h. The Pt/γ-alumina (*11*) and Pt/zirconia (*7*) samples were prepared previously by an analogous multiple impregnation method. The metal concentration range on the three supports is as follows: 0.03–10 wt% Pt/γ-alumina, 0.04–1.5 wt% Pt/zirconia, and 0.10–4.76 wt% Pt/silica. Standard pretreatment for all catalysts, after calcination in air at 600°C, consisted of reduction in hydrogen at 400°C for 2 h followed by exposure to oxygen at 500°C for 20 h.

The BET surface areas for the three metal oxides after calcination, as determined from nitrogen adsorption at liquid nitrogen temperature, were 85.5, 5.5, and 223.6 m^2/g for γ-alumina, zirconia, and silica, respectively. The platinum dispersion (fraction of Pt surface atoms) was determined by CO adsorption at room temperature. The samples were first reduced in hydrogen at 400°C for 1 h and then thoroughly evacuated while cooling to room temperature. The adsorption measurements were carried out with a conventional glass apparatus equipped with calibrated bulbs and a quartz-glass spiral manometer. Helium was used to measure the volume of the adsorption vessel not occupied by the sample. An adsorption stoichiometry of $CO_{(adsorbed)}$: $Pt_{(surface\ atom)}$ = 0.7 was used in the calculations (*12*), assuming that this ratio is valid for all three supports. Table 1 lists the dispersion values calculated accordingly for the catalyst samples.

TABLE 1

Metal Dispersion as a Function of Pt Concentration

Support	Pt concentration (wt%)	Dispersion	Reference
γ-Alumina			
	0.03	1.09	(*11*)
	0.05	1.00	Present study
	0.12	0.97	(*11*)
	0.40	1.15	(*11*)
	1.40	0.73	(*11*)
	5.00	0.33	(*11*)
	10.0	0.20	(*11*)
	9.17	0.04	Present study
Zirconia			
	0.04	1.00	(*7*)
	0.10	0.38	(*7*)
	0.81	0.20	(*7*)
	1.50	0.08	(*7*)
Silica			
	0.10	0.77	Present study
	0.50	0.43	Present study
	4.76	0.03	Present study

Catalyst Sulfation

Catalyst sulfation was carried out by two methods to compare changes attributable to the sulfur source. The first technique consisted of catalyst exposure to flowing sulfur dioxide in excess oxygen (O_2/SO_2 = 3) at 500°C for 5 h. In the second approach, approximately 10 g of catalyst was continuously stirred with 50 ml of 1.1 *N* H_2SO_4 at room temperature for about 2 h. After treatment with sulfuric acid, the catalysts were filtered, washed with distilled water and dried in air at 120°C for 5 h. The samples used in the acid strength measurements were then calcined in air at 400°C for 2 h. For the activity studies, the sulfated catalysts were pretreated by reduction in hydrogen followed by exposure to oxygen, as explained earlier. It is assumed that the samples are fully sulfated under the stated conditions since additional exposure to sulfur did not alter the activity beyond what was initially observed.

For γ-alumina, the development of sur-

face sulfate from exposure to a SO_2/O_2 mixture has been confirmed by infrared spectroscopy (*13*). Water-insoluble aluminum salts are formed after treatment of γ-alumina with sulfuric acid (*14*). Analogously, surface sulfate is produced on zirconia after SO_2 oxidation or contact with H_2SO_4 (*8, 9*). Conversely, silica does not form sulfate when exposed to either sulfur dioxide or sulfuric acid (*8, 9*).

Acid Strength Measurements

The change in total acid strength upon catalyst sulfation was measured qualitatively with Hammett indicators. Briefly, the Hammett indicator method involves reacting nonaqueous neutral bases of known pK_a with the catalyst surface (*15*). The neutal base and conjugate acid differ in color. By observing the color of the adsorbed indicator it can be determined whether the catalyst surface is of sufficient acid strength to convert the neutral base into its conjugate acid. Indicators of increasing pK_a are used until the adsorbed indicator remains in its basic form and thus, a maximum surface acid strength can be determined. The Hammett indicator function, H_0, is typically used in reporting acid strength data with H_0 defined as the inverse logarithm of the dissociation constant, K_a. Table 2 is a list of the indicators used in the study. The indicators range in acidity over 20 orders of magnitude from bromothymol blue, $H_0 = +7.2$, to 2,4-dinitrofluorobenzene, $H_0 = -14.5$.

The acid strength of γ-alumina is increased upon sulfation (*14, 16–18*). If amorphous zirconia is exposed to sulfur, superacid sites ($H_0 \leq -12$) are generated (8, 9, 19, 20). The zirconia employed in this study is monoclinic (*21*) and it was of interest to observe the influence of sulfation on this crystalline material.

Activity Studies

Propane oxidation served as a model reaction to compare catalyst activity. Two different reactors, a recirculation batch and an integral flow system, were used for the activity measurements. In the first series of measurements, obtained in the absence of sulfur, a batch reactor (*22*) was employed which is a preferred configuration to measure kinetic parameters free of mass and heat transfer limitations. The maximum flow rate of the recirculation system, however, was not sufficient to maintain isothermal conditions in all instances. Uncontrolled thermal excursion, resulting in autogenous rather than preselected reaction conditions, necessitated the additional use of an integral flow system. Light-off curves, even if they are measured under steady-state conditions are encumbered by temperature and concentration gradients created by self-generated thermal conditions. Empirically, light-off curves usually can be closely approximated by a sigmoidal curve,

$$c = \frac{1}{1 + \exp[-a(T - T_{50})]}, \qquad (1)$$

where $c(T)$ describes the conversion of a selected reactant as a function of temperature, T. The temperature at 50% conversion, T_{50}, is a measure for catalyst activity. The slope of the light-off curve depends on the parameter a, which is comprised of several material constants relating to thermodynamic and heat-transfer properties. These properties are commonly ignored when catalyst activity is described by T_{50}. However, subtle differences in catalyst structure sometimes seem to produce significant variations in light-off characteristics and even hysteresis may be found between heating and cooling cycles. Figures 2 and 3 in a report by Shelef *et al.* (*23*) exemplify such changes in the shape of light-off curves for different metal oxides deposited on a support consisting of 95% γ-alumina and 5% silica. A comparison of isothermal reaction rates measured in the batch mode and steady-state rates obtained from light-off curves has obvious limitations. While both reactor systems can be expected to show agreement in the relative ranking of catalysts with substantially different activities, they may yield seemingly different results

TABLE 2

Hammett Indicators

Indicator	H_0	K_a
Bromothylmol blue (3′,3″-Dibromothymolsulfonephthalein)	+7.2	6.31×10^{-8}
Neutral red (basic red, C.I. 50040)	+6.8	1.58×10^{-7}
Methyl red {2-[4-(dimethylamino)phenylazo]benzoic acid}	+4.8	1.58×10^{-5}
4-Phenylazoaniline	+2.8	1.58×10^{-3}
4-(Phenylazo)diphenylamine	+1.5	3.16×10^{-2}
4-Nitroaniline	+1.1	7.94×10^{-2}
2-Nitroaniline	−0.2	1.58×10^{0}
4-Chloro-2-nitroaniline	−0.9	7.94×10^{0}
4-Nitrodiphenylamine	−2.4	$2.51 \times 10^{+2}$
2,4-Dichloro-6-nitroaniline	−3.2	$1.58 \times 10^{+3}$
4-Nitroazobenzene	−3.3	$2.00 \times 10^{+3}$
2,6-Dinitro-4-methylaniline	−4.3	$2.00 \times 10^{+4}$
2,4-Dinitroaniline	−4.4	$2.51 \times 10^{+4}$
N,*N*-Dimethyl-2,4,6-trinitroaniline (soln. in conc. H_2SO_4)	−4.7	$5.01 \times 10^{+4}$
Chalcone	−5.6	$3.98 \times 10^{+5}$
2-Benzoylnapthalene	−5.9	$7.94 \times 10^{+5}$
4-Benzoylbiphenyl	−6.2	$1.58 \times 10^{+6}$
2-Bromo-4,6-dinitroaniline	−6.6	$3.98 \times 10^{+6}$
Anthraquinone	−8.1	$1.26 \times 10^{+8}$
2,4,6-Trinitroaniline (soln. in conc. H_2SO_4)	−9.3	$2.00 \times 10^{+9}$
4-Nitrotoluene	−11.3	$2.00 \times 10^{+11}$
2,4-Dinitrotoluene	−13.7	$5.01 \times 10^{+13}$
2,4-Dinitrofluorobenzene	−14.5	$3.16 \times 10^{+14}$

for minor variations. This common limitation in correlating catalyst performance described by fundamental parameters on the one hand, and practical light-off curves, on the other, obviously manifests a bothersome deficiency.

(*a*) *Batch recirculation reactor.* A vertical reactor vessel was used for both reactor systems. It had a volume of about 150 cm^3 and contained the powdered samples on a quartz-glass fritted disk. Further details of the batch system are given elsewhere (*22*). Each sample contained the same amount of Pt (1 mg) in order to compare changes in activity with particle size. The activity data were recalculated to represent 4 mg of Pt for comparison with earlier studies (*7, 11*). The reactant mixture consisted of 10 Torr propane, 120 Torr oxygen, and 520 Torr argon (1 Torr = 133.3 N/m^2). Initially, the reactants were circulated, by-passing the reactor, for 20 min to achieve complete mixing. The mixture was then passed through the preheated-evacuated reactor. The propane concentation remaining in the gas phase was measured as a function of time. Data were recorded after adsorption equilibrium betwen the gas-phase and the catalyst had been established within 10 min.

(*b*) *Integral flow reactor.* As mentioned above, an integral flow reactor had to be employed when isothermal reaction conditions could not be maintained in the batch system. To ensure the same flow resistance and to keep the reactant mixture from by-passing the catalyst, each sample contained the same amount of Pt (1 mg) which was then diluted to 2.5 g by admixing blank powders of γ-alumina, zirconia, or silica. The propane-oxidation activity of the blank supports was measured for comparison with samples containing platinum and was found to be negligible. Space-velocity and heating rate were adjusted to provide steady-state

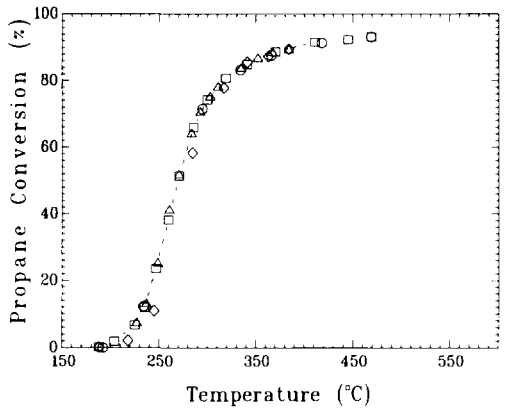

FIG. 1. Reproducibility of steady-state propane oxidation over 0.04 wt% Pt/zirconia, measured with increasing (○, □) and decreasing (◇, △) temperature.

conditions. The flow mixture consisted of 5 cm^3/min propane, 70 cm^3/min oxygen, and 1300 cm^3/min argon. Propane conversion was recorded as a function of temperature in the range from 150 to 500°C. An exposed thermocouple wire was placed in contact with the catalyst. Data collected during heating and cooling cycles showed good reproducibility and were free of hysteresis, as shown in Fig. 1.

(*c*) *Gas analysis*. The gas samples were analyzed by injecting volumes of about 1 cm^3 into a mass spectrometer (VG Quadrupoles). The peaks monitored were *m/e* 29 (propane, fragmentation peak), *m/e* 32 (oxygen, parent peak), *m/e* 40 (argon, parent peak),and *m/e* 44 (carbon dioxide, parent peak). The contribution of propane to *m/e* 44 was calibrated and subtracted. The absolute amounts of the gas components were based on the known pressure of argon. The basic calibration of the mass spectrometer was carried out with pure propane, oxygen, argon, and carbon dioxide. The complete oxidation of propane to carbon dioxide and water accounted for 95% of the propane consumption as determined by the carbon balance.

RESULTS AND DISCUSSION

Acid Strength Measurements

The results of the acid strength measurements, derived from Hammett indicators, are listed in Table 3. In order to correctly observe the color of the adsorbed indicator the samples had to be initially white. Hence, only the blank supports and the catalysts of lowest platinum concentration are shown. The catalysts of higher metal loading were brownish and it was difficult to determine the hue of the adsorbed indicator. As stated previously, two different methods were employed to sulfate the catalysts: exposure to a SO_2/O_2 mixture and contact with 1.1 *N* sulfuric acid. The treatment is reflected in the nomenclature of Table 3 by the suffixes $-SO_2$ and $-H_2SO_4$, respectively.

Prior to sulfation, the acid strengths of γ-alumina and zirconia were identical, $H_0 \geq +4.8$, as defined by methyl red. Sulfation of γ-alumina produced a moderate increase in acid strength to $H_0 \geq +1.1$. A difference can be noted in the sulfated γ-alumina samples, $-SO_2$ and $-H_2SO_4$; however, it is relatively small and corresponds to adjacent indicators in the Hammett series. In contrast to

TABLE 3

Summary of Acid Strength Measurements

Catalyst	H_0	K_a
Al_2O_3	+4.8	1.58×10^{-5}
Al_2O_3–H_2SO_4	+1.5	3.16×10^{-2}
Al_2O_3–SO_2	+1.1	7.94×10^{-2}
$Al_2(SO_4)_3$ (bulk)	+1.1	7.94×10^{-2}
0.05 wt% Pt/Al_2O_3	+4.8	1.58×10^{-5}
0.05 wt% Pt/Al_2O_3–H_2SO_4	+1.5	3.16×10^{-2}
0.05 wt% Pt/Al_2O_3–SO_2	+1.1	7.94×10^{-2}
ZrO_2	+4.8	1.58×10^{-5}
ZrO_2–H_2SO_4	−5.6	$3.98 \times 10^{+5}$
ZrO_2–SO_2	−5.6	$3.98 \times 10^{+5}$
$Zr(SO_4)_2$ (bulk)	−2.4	2.51×10^{-2}
0.04 wt% Pt/ZrO_2	+4.8	1.58×10^{-5}
0.04 wt% Pt/ZrO_2–H_2SO_4	−5.6	$3.98 \times 10^{+5}$
0.04 wt% Pt/ZrO_2–SO_2	−5.6	$3.98 \times 10^{+5}$
SiO_2	+7.2	6.31×10^{-8}
SiO_2–H_2SO_4	+7.2	6.31×10^{-8}
SiO_2–SO_2	+7.2	6.31×10^{-8}
0.10 wt% Pt/SiO_2	+7.2	6.31×10^{-8}
0.10 wt% Pt/SiO_2–H_2SO_4	+7.2	6.31×10^{-8}
0.10 wt% Pt/SiO_2–SO_2	+7.2	6.31×10^{-8}

γ-alumina, zirconia exhibits a greater increase in acid strength, $H_0 \geq -5.6$, after sulfation by either SO_2 oxidation or H_2SO_4 exposure. Thus, for crystallized zirconia, sulfation increases the surface acidity but not to the level of a superacid, which is observed with amorphous zirconia (*8, 9, 19, 20*). The surface acid strength of silica remains unchanged at $H_0 \geq +7.2$ after sulfation (Table 3). Recall, silica does not form a surface sulfate by SO_2 oxidation or contact with H_2SO_4 (*8, 9*).

Batch Experiments

Figure 2 is a semilogarithmic plot of the decrease in gas-phase propane with time for 0.10 wt% Pt/silica at 230, 275, and 310°C. The linearity of the data illustrates that propane oxidation can be described as first order in propane under the experimental conditions selected. The rate constant is obtained from the slope of the reaction isotherm from 10–90 minutes. The data were analyzed in this fashion in order to compare previous propane oxidation results from our laboratory for platinum supported on γ-alumina (*11*) and on zirconia (*7*). The apparent activation energy, derived from the temperature dependence of the rate constant, was independent of metal concentration and support material. The measured values are 22.1 ± 3.4, 17.8 ± 3.5, and 16.6 ± 3.8 kcal/mol for Pt/γ-alumina (*11*), Pt/zirconia (*7*), and Pt/silica, respectively. Within experimental error, these results are in agreement with each other and with literature data for the same catalytic reaction over platinum which range from 17 to 25 kcal/mol (*24, 25*).

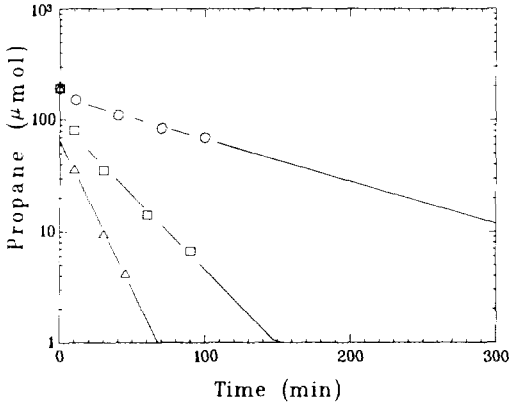

FIG. 2. Propane oxidation over 0.10 wt% Pt/silica at (○) 230, (□) 275, and (△) 310°C.

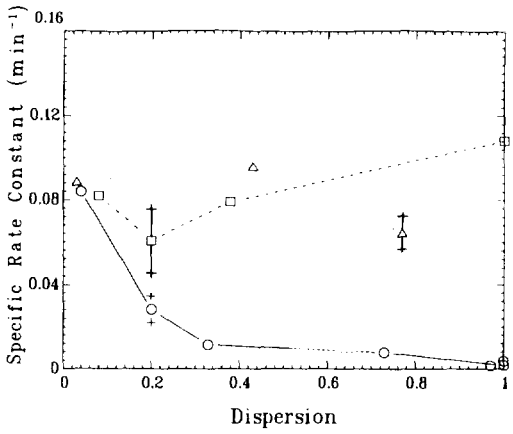

FIG. 3. Specific rate constant of propane oxidation at 275°C as a function of Pt dispersion over Pt/γ-alumina (○), Pt/zirconia (□) and Pt/silica (△). Error limits are shown for each series.

For each support the platinum loadings were chosen to represent changes in reaction kinetics attributable to extremes in particle size. Activities of catalysts of high dispersion ($D \sim 1$) are expected to be more dependent on the support material, since a majority of metal atoms are in direct contact with the support. As the platinum concentration is increased and the metal particles grow in size, effects due to a metal–support interaction are expected to fade. The specific rate constant of platinum supported on silica is plotted in Fig. 3 as a function of metal dispersion together with data obtained in earlier studies (*7, 11*). Note that the specific rate constant is derived from the rate constant measured at 275°C (Fig. 2) adjusted to represent 4 mg bulk Pt and divided by the metal dispersion (Table 1) and thus, represents a turnover rate. The error bars shown in Fig. 3 indicate the data scatter associated with the measured rate constant. Focusing on the samples of lowest metal

dispersion, corresponding to the largest particle size, the specific rate constant of propane oxidation over platinum is the same for the three support materials, γ-alumina, zirconia, and silica. Conversely, the activity of platinum at high metal dispersions, obtained at low metal loadings, can be greatly influenced by the support. Thus, the specific rate constant for fully dispersed platinum ($D = 1$) is 30 times higher for zirconia than for γ-alumina. This observation is consistent with the fact that γ-alumina is a more reactive support compared to zirconia (*26*). The interaction of small platinum clusters with γ-alumina is also evident from other analytical methods such as temperature-programmed reduction (*27*), X-ray photoelectron spectroscopy (*28*), and Raman spectroscopy (*29*), whereas larger supported particles behave similar to bulk platinum. The activity data suggest that a large fraction of platinum atoms in contact with γ-alumina is deactivated by a metal-support interaction.

At a relatively high dispersion, $D = 0.77$, the specific rate constant with respect to surface platinum is about 20 times greater for Pt/silica than for fully dispersed Pt/γ-alumina. The oxidation activity of Pt/zirconia is slightly higher compared to Pt/silica at 275°C.

Flow Experiments

The flow experiments were conducted on selected catalysts, specifically those samples which had the highest and lowest platinum dispersions on each support (Table 1). For reasons given earlier, the flow experiments are intrinsically less suited to measure catalyst activity reliably, as compared to the batch experiments.

(*a*) *Pt/γ-alumina.* Figure 4 is a graph of propane conversion versus temperature over γ-alumina containing 0.05 wt% platinum before and after sample sulfation. The light-off temperature decreases in the order $Pt/\gamma\text{-}Al_2O_3 > Pt/\gamma\text{-}Al_2O_3\text{–}H_2SO_4 > Pt/\gamma\text{-}Al_2O_3\text{–}SO_2$. The temperatures of 50% conversion for these three samples are 390, 285, and 250°C, respectively. The greatly enhanced activity upon sulfation confirms earlier results from this laboratory (*4*, *6*). At a constant activation energy of 22.1 kcal/mol, a shift in T_{50} from 285 to 250°C for the SO_2 treated Pt/γ-alumina compared to the H_2SO_4-soaked specimen corresponds to a rate increase by almost a factor of 4. This activity difference remains presently unexplained, however, one could speculate that the oxidation of SO_2 on platinum preferentially creates sulfate groups on γ-alumina close to platinum, while sulfate produced by soaking with sulfuric acid is nonspecific with respect to the catalyst surface. Nevertheless, the difference seems to be associated with both T_{50} and the steepness of the light-off curve (parameter a in Eq. (1)) and is discussed in a later section. Within the experimental error of 3 kcal/mol in the activation energy and the uncertainties inherent to light-off curves, the activity increase upon sulfation is consistent with an increase in the density of active sites; it is not necessary to invoke a lowering in activation energy.

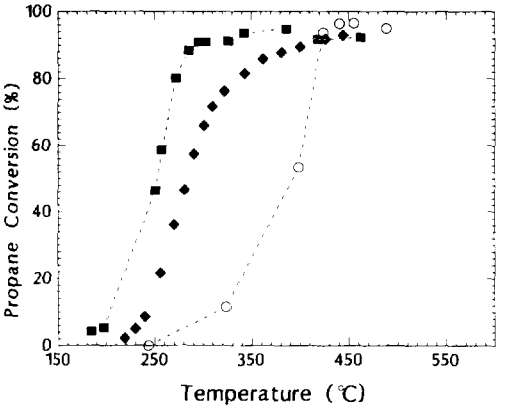

FIG. 4. Propane oxidation over 0.05 wt% Pt supported on γ-alumina: untreated (○), treated with SO_2 (■), and H_2SO_4 (◆).

The effect of metal loading on propane oxidation measured in the integral flow reactor is illustrated by the data in Table 4. The activities listed in Table 4 are expressed in two ways; as the temperature required for

TABLE 4

Results from Flow Studies

Catalyst	Temp. at 50% C_3H_8 Conv. (°C)	Conv. at T = 350°C
γ-Al_2O_3	550	0%
γ-Al_2O_3–SO_2	525	8%
0.05 wt% Pt/γ-Al_2O_3	390	26%
0.05 wt% Pt/γ-Al_2O_3–H_2SO_4	285	84%
0.05 wt% Pt/γ-Al_2O_3–SO_2	250	91%
9.17 wt% Pt/γ-Al_2O_3	350	50%
9.17 wt% Pt/γ-Al_2O_3–SO_2	275	86%
ZrO_2	—	0%
ZrO_2–SO_2	—	4%
0.04 wt% Pt/ZrO_2	283	81%
0.04 wt% Pt/ZrO_2–H_2SO_4	283	85%
0.04 wt% Pt/ZrO_2–SO_2	275	86%
0.81 wt% Pt/ZrO_2	315	70%
0.81 wt% Pt/ZrO_2–SO_2	255	90%
SiO_2	—	2%
SiO_2–SO_2	—	2%
0.10 wt% Pt/SiO_2	305	72%
0.10 wt% Pt/SiO_2–SO_2	290	82%
4.76 wt% Pt/SiO_2	250	82%
4.76 wt% Pt/SiO_2–SO_2	240	87%

50% propane conversion and as the conversion measured at 350°C. Over unsulfated γ-alumina, propane-oxidation activity increases with metal concentration. Thus, for 9.17 wt% Pt, a temperature of 350°C is required for 50% propane conversion, which is 40°C lower than that needed for 0.05 wt% Pt for the same conversion. Considering the low metal dispersion of 9.17 wt% Pt/γ-alumina (D = 0.04), the result indicates that expressed per Pt surface atom, this sample is about 50 times more active than 0.05 wt% Pt/γ-alumina. The result is in agreement with the change in specific rate constant measured by the batch reactor (Fig. 3). Sulfation enhances the activity for both platinum loadings, as shown in Table 4. In the absence of platinum, the γ-alumina support, with or without sulfate, has to be heated above 500°C to show any propane-oxidation activity.

(*b*) *Pt/zirconia.* Figure 5 is a plot of propane conversion as a function of temperature for 0.04 wt% Pt/zirconia exposed to SO_2, H_2SO_4, and untreated. Unlike Pt/γ-alumina, no clear change in activity is evident, in spite of the fact that surface sulfate is formed on zirconia after exposure to sulfuric acid and sulfur dioxide (*8, 9*) and is evident from the markedly enhanced acid strength of the surface (Table 3).

The effect of metal loading or particle size on propane activity is illustrated by Fig. 3 (batch experiments) and Table 4 (flow experiments). Over a constant amount of Pt (1 mg), the larger particles of 0.81 wt% Pt/zirconia (D = 0.20) require 315°C to achieve 50% propane conversion, while the fully dispersed smaller particles of 0.04 wt% Pt/zirconia (D = 1.0) appear to be more active as indicated by a corresponding lower temperature of 283°C (Table 4). When calculated per Pt surface atom, however, the activity is thought to remain constant, within the experimental error, consistent with the batch-reactor data (Fig. 3).

Sulfation distinctly enhanced the propane-oxidation activity for 0.81 wt% Pt/zirconia. This is described in Table 4 by a reduction in the temperature of 50% conversion by 60°C compared to the sample free of sulfate. The flow-reactor data suggest that the sulfation is more beneficial at the higher platinum loading. Without additional data, explanations for the preferential improvement for larger platinum particles supported on zirconia remain speculative.

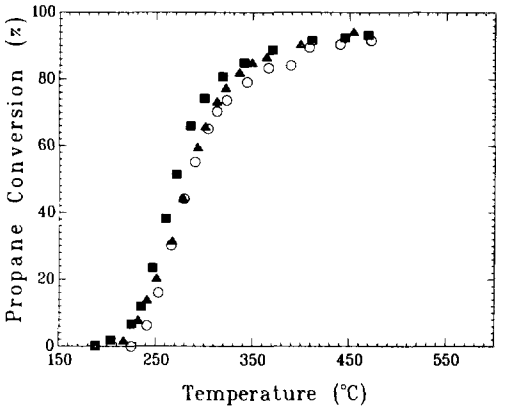

FIG. 5. Propane oxidation over 0.04 wt% Pt supported on zirconia: untreated (○), treated with SO_2 (■), and H_2SO_4 (◆).

(*c*) *Pt/silica.* The flow-reactor results for 0.10 wt% Pt/silica before and after the sulfation treatment are shown in Fig. 6. Silica does not form a surface sulfate either by exposure to H_2SO_4 or a SO_2/O_2 mixture (*8, 9*). Below 20 and above 85% conversion the activity curves are the same. However, between these two points, propane conversion increases more steeply with temperature after sulfation. Several experimental runs were conducted and the data shown in Fig. 6 are representative of the activity difference between the unsulfated and sulfated catalyst. Therefore, although silica does not form a surface sulfate with the methods employed in this study, it appears that a SO_2/O_2 atmosphere at 500°C affects those properties of the catalyst which determine the slope of the light-off curve. A difference of 15°C between the parameter T_{50} of the two light-off curves in Fig. 6 is therefore considered to be unimportant and typical for unexplained variations in light-off characteristics.

For Pt/SiO_2, the batch-reactor data in Fig. 3 indicate a slight increase in activity with increasing particle size (decreasing dispersion). However, this change is small and cannot be clearly separated from data scatter attributable to experimental error. On the other hand, data in Table 4 and the light-off curves in Fig. 7 yield a more substantial activity increase with particle size, manifest by a decrease in T_{50} by about 50°C in the concentration range from 0.10 to 4.76 wt% Pt/SiO_2. The activity difference displayed by the light-off curves in Fig. 7 is emphasized by a substantial change in slope, as discussed below.

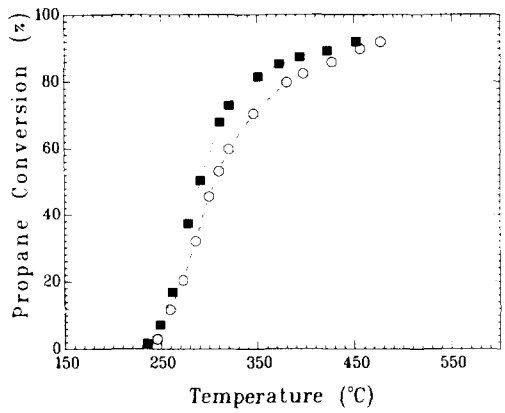

FIG. 6. Propane oxidation over 0.10 wt% Pt on silica: untreated (○) and treated with SO_2 (■).

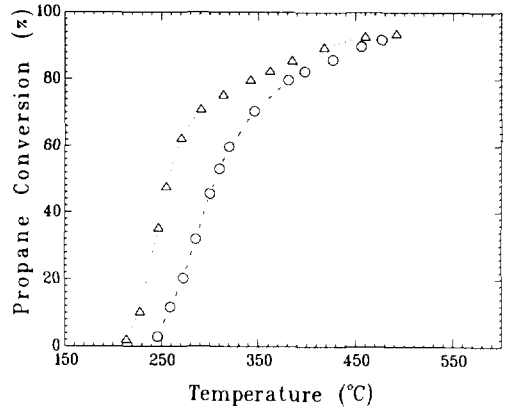

FIG. 7. Propane oxidation over Pt/silica: 0.10 wt% (○) and 4.76 wt% (△).

Comments on Apparent Activity Differences

Differences in reactivities resulting from the particulars of a reactor technique are bothersome and create an obvious dilemma. While a gradientless batch reactor is best suited for studying fundamental kinetics, catalytic converters employed in automotive emission control are integral flow reactors, with an intrinsic variability in the transfer of heat and mass that can profoundly affect steady-state conversions. The predicament is usually not obvious since the two reactor systems are rarely used simultaneously to describe catalyst performance. Two examples from the current investigation are selected to illustrate this obstacle.

While both reactor systems yield the same activity ranking for highly dispersed platinum on the three supports examined, γ-alumina < silica < zirconia, they produce different results for large platinum particles.

The batch-reactor data (Fig. 3) show the same activity per surface Pt, irrespective of support, as one would expect. In contrast, the flow reactor activities over large platinum particles follow the ranking γ-alumina < zirconia < silica, as indicated by the light-off curves in Fig. 8. This difference is not easily explained, even if additional plausible structure variations are considered ad hoc in the activity analysis, such as the true metal dispersion under reaction conditions. Note that the sigmoidal light-off curves in Fig. 8 differ in their slopes, and the higher activity (given by a lower T_{50}) is associated with a steeper ascent. Thus, when the slope is expressed in terms of the parameter a (Eq. (1)), values of 0.08 and 0.03 are obtained for 4.76% Pt/SiO_2 and 9.17 wt% Pt/Al_2O_3, respectively. Were the slopes identical, the observed differences in the light-off curves would be significantly diminished.

Figure 9 provides a second example of the inherent complications associated with light-off curves. In Fig. 4, a substantial difference exists in the light-off curves for Pt/γ-alumina treated with SO_2 and H_2SO_4. These curves are reproduced in Fig. 9 by the dashed and solid curves, respectively. When the propane-conversion data measured over 0.81 wt% Pt/ZrO_2-SO_2, are added to the figure (circles) the points straddle both

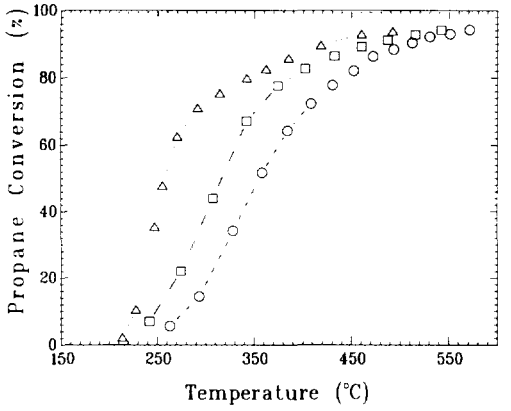

FIG. 8. Propane oxidation over 9.17 wt% Pt/γ-alumina (○), 0.81 wt% Pt/zirconia (□), and 4.76 wt% Pt/silica (△).

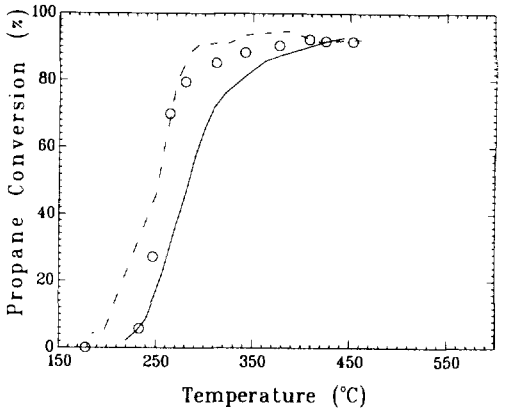

FIG. 9. Propane oxidation over Pt: 0.05 wt% Pt/γ-alumina treated with SO_2 (---) and H_2SO_4 (———), and 0.81 wt% Pt/zirconia treated with SO_2 (○).

light-off curves. At lower and higher temperatures the points coincide with the dashed curve, while in the middle range, near 250°C, they coincide with the solid curve. These results illustrate that a change in the light-off characteristics, reflected by an ill-defined slope, can have a pronounced effect on the activity parameter T_{50} and thus, result in misleading conclusions about true activity changes. Despite the limitations of the light-off curves the following observations can be drawn from the experimental evidence.

CONCLUSIONS

1. For highly dispersed platinum, propane-oxidation activity decreases in the order zirconia > silica > γ-alumina. This series suggests a substantial deactivation by a strong interaction between platinum and γ-alumina. The relative propane-oxidation activities are supported by batch and flow reactor results.

2. The activity of large platinum particles, obtained at high metal loadings, results in conflicting data. While propane oxidation measured earlier in a recirculation-batch reactor yielded the same turnover rate on the three supports, flow-reactor experiments show an apparent activity decrease in the order silica > zirconia > γ-alumina.

3. On highly dispersed Pt/γ-alumina, sulfating substantially increases the propane-oxidation rate. The same sulfur treatment of comparable platinum samples supported on zirconia or silica has no significant effect on the turnover rate of propane oxidation. The overall oxidation rate also increases over larger platinum particles after sulfation on γ-alumina and zirconia, but not on silica.

4. Sulfation of the three supports results in an increase in surface acid strength for zirconia, a moderate increase for γ-alumina and no increase for silica. Thus, surface acid-strength, for the catalysts employed in this study, is not the major contributing factor on the oxidation rate of propane.

5. The change in catalyst activity either by the support material or by surface sulfate appears to be primarily caused by a modification in reaction-site density, as changes in the apparent activation energy, beyond the experimental error, were not found.

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