JOURNAL OF CATALYSIS **139**, 268–276 (1993)

Propane Oxidation over Platinum Supported on Zirconia

C. P. HUBBARD,* K. OTTO,†,[1] H. S. GANDHI,† AND K. Y. S. NG*

**Chemical Engineering Department, Wayne State University, 5050 Anthony Wayne Dr., Detroit, Michigan 48202; and †Research Staff, Ford Motor Company, Dearborn, Michigan 48121-2053*

Received March 13, 1992; revised August 5, 1992

Propane oxidation activity over Pt/zirconia was studied as a function of metal concentration, metal surface area, and temperature. The catalysts, prepared by multiple impregnation of zirconia with chloroplatinic acid, ranged in concentration from 0.02 to 1.5 wt% Pt. A recirculation batch reactor was used for the activity experiments. At a fixed amount of Pt (4 mg), the oxidation rate decreased by a factor of 20 with increasing metal concentration. When calculated per Pt surface atom, as determined by CO chemisorption, the specific oxidation rate initially decreased and then reached a constant value at concentrations above 0.10 wt% Pt. The apparent activation energy remained constant at 17.8 ± 3.5 kcal/mol with Pt concentration. To evaluate the effect of support material, the data were compared to an analogous study in our laboratory over Pt/γ-alumina. Over highly dispersed platinum, propane oxidation activity was two orders of magnitude faster over Pt/zirconia as compared to Pt/γ-alumina. The activity change reflects a difference in interaction between support and catalytic metal. At higher Pt concentrations the influence of the support vanishes and the rate constants on both supports are the same, as expected. At lower Pt concentrations, metal redispersion occurs readily in oxygen at 500°C on γ-alumina, but not on zirconia, according to observed changes in propane oxidation rate.

INTRODUCTION

Hydrocarbon (HC) oxidation is of continued interest in the automotive industry because of stricter government emission standards. Alkane oxidation compared to other hydrocarbons, for example alkenes, is relatively slow (*1*). Hence, while the total HC concentration decreases as the exhaust passes through the catalytic converter, the fraction of low-molecular weight alkanes increases. For example, Sigsby *et al.* (*2*) reported that the alkane fraction at the catalyst outlet had increased by about 30% compared to the inlet. Thus, in order to meet projected standards for HC emissions, a better understanding is needed of the parameters which influence the inherently slow oxidation of short-chain alkanes. This investigation addresses differences in activity which are associated with a change in Pt loading (dispersion), thermal treatment, and support material by comparing zirconia and γ-alumina supports.

Previous investigations of alkane oxidation over Pt catalysts have focused on the unsupported metal (*3, 4*) and on γ-alumina (*5, 6*) or ceria/γ-alumina (*6*) supports. These studies concluded that the propane oxidation rate, calculated per Pt surface atom, is dependent on metal loading. In other words, propane oxidation over Pt behaves as a structure sensitive reaction. It has been shown for the Pt/γ-alumina system that small metal clusters, which exist at low metal concentrations, exhibit properties much different from those of higher metal concentration, which resemble bulk metal (*7–9*). The question arises as to whether the difference between small clusters and larger crystalline particles is caused by a change in particle properties or by a metal–support interaction. Independent of the support, small metal clusters are inherently different from bulk-like particles. It is known that

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

small clusters consisting of 50 to 100 atoms exhibit different crystallographic planes and possess different physical properties, such as melting temperature, compared to the bulk solid (*10*). For even smaller unsupported clusters, containing less than 25 atoms, nonmonotonic fluctuations have been reported when changing the cluster size by one atom at a time (*11, 12*). The support material may, depending on its own characteristics and properties, influence catalytic activity for highly dispersed metals in direct contact with the support. As the metal concentration is increased and the particles begin to grow the influence of the support is expected to decrease. Clearly, it is difficult to analyze the basic differences in activity of small metal clusters and larger bulk-like particles, especially since the support material itself may influence the topography and energetics of the catalytic metal.

Recently, methane oxidation was compared over Pt/zirconia and Pt/γ-alumina (*13*). For highly dispersed Pt the oxidation rate was about 10 times faster over Pt/zirconia compared to Pt/γ-alumina. A possible explanation for the rate difference is that zirconia is a less reactive support compared to γ-alumina (*14*). Methane oxidation, however, proceeds through a different reaction mechanism compared to higher alkanes because of the lack of a C–C bond. It is of interest to study whether the influence of the support observed for methane oxidation (*13*) is also observed for higher alkanes. In the current study propane oxidation was chosen as a model for alkane oxidation. Zirconia was used as a support material for Pt. The results are compared to an analogous study in our laboratory on Pt/γ-alumina (*5*) to assess the influence of the support material, metal concentration, and pretreatment conditions.

EXPERIMENTAL

The zirconia used in the study was a high-temperature "ceramic grade" material obtained from Aldrich. It was highly crystalline and had a monoclinic structure as indicated by X-ray diffraction (*15*). The BET surface area, as determined by nitrogen adsorption at liquid nitrogen temperature, is 5.5 m^2/g. The catalysts were prepared by saturating the well-stirred zirconia with approximately one-half of the desired amount of chloroplatinic acid. The samples were dried at 120°C for 2 h in air, followed by a repeat impregnation with the remaining Pt solution. The catalysts were again dried at 120°C for 2 h and finally calcined at 600°C for 20 h. The concentration range was 0.02–1.5 wt% Pt. The pretreatment was kept constant for all samples with reduction in hydrogen at 400°C for 2 h, followed by exposure to oxygen at 500°C for 20 h. The above procedure is analogous to the method used in the synthesis of the Pt/γ-alumina samples (*5*).

A recirculating batch system was used for the activity measurements. The total volume of the system was about 500 cm^3, with a reactor volume of approximately 150 cm^3. Details of the glass apparatus are described elsewhere (*16*). The reactant mixture consisted typically of 10 Torr propane, 120 Torr oxygen, and 520 Torr argon (1 Torr = 133.3 Pa). Pressures were measured by a quartz spiral manometer. The initial mixture was recirculated through the system, bypassing the reactor, for at least 20 min to allow complete mixing. At a predetermined time the stopcocks to the evacuated heated reactor were opened and the gases were passed through the powdered catalyst which was suspended on a quartz-glass fritted disk. A glass-enclosed thermocouple was positioned directly above the sample to measure the reaction temperature. In the initial experiments, each sample contained 4 mg Pt, as in the case of the Pt/γ-alumina study (*5*). However, mass-transfer problems developed because of the large amount of sample required for 0.02–0.04 wt% Pt/zirconia. Thus, for these catalysts a constant amount of sample (1 g) was used with the data normalized to represent 4 mg Pt. To check the validity of this procedure, the activity experiments for 0.1–1.5 wt% Pt/zirconia were repeated using a 1-g sample. The data from both sets of experiments were in good agreement. Thus, compatible data are reported on the basis of 1-g sample size, adjusted to represent 4 mg Pt.

Data points for the activity curves were obtained with a mass spectrometer (VG Quadrupoles) which was initially calibrated with pure propane, oxygen, carbon dioxide, and argon. A sample (1 cm^3) was injected into the mass spectrometer to measure the gas composition as a function of time. The mass peaks monitored were *m/e* 29 (fragmentation peak, propane), *m/e* 32 (parent peak, oxygen), *m/e* 40 (parent peak, argon), and *m/e* 44 (parent peak, carbon dioxide). The contribution of propane to the *m/e* 44 peak was determined and subtracted. Argon (*m/e* 40) was used as a reference for peak intensities. Based on the fixed amount of argon the concentrations of reactants and products were determined. Thus, the consumption of propane (*m/e* 29) in the gas phase was monitored as a function of time. Under the standard experimental condition of excess oxygen ($O_2 : C_3H_8 = 12 : 1$) the end product of the carbon consumed consisted of at least 95% CO_2, as determined by the carbon balance and also, by comparison of the amounts of propane and oxygen reacted. The amount of CO was considered to be negligible since the peak at *m/e* 28 was fully accounted by background nitrogen and CO_2 fragmentation. The amount of surface Pt was measured volumetrically by CO chemisorption at room temperature on samples reduced in hydrogen at 400°C and thoroughly evacuated *in situ*. A conventional glass vacuum apparatus was used for the volumetric measurements. The pressure was measured by a quartz spiral manometer. The unoccupied volume of the adsorption vessel was measured by helium expansion from a calibrated volume.

RESULTS AND DISCUSSION

Propane Oxidation Rates over Pt/Zirconia

The rate of propane oxidation over bulk (*4*) and supported (*5*) Pt has been described as first order with respect to propane concentration and independent of oxygen pressure provided an excess of oxygen gas is used. For the current study the initial reactant mixture consisted of propane and oxygen at a ratio $O_2 : C_3H_8 = 12 : 1$. The complete oxidation of propane to carbon dioxide requires a ratio of $O_2 : C_3H_8 = 5 : 1$.

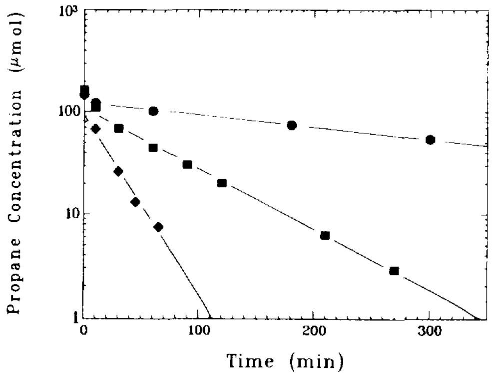

FIG. 1. Reaction isotherms of propane oxidation on 0.81 wt% Pt/zirconia at (●) 230°C, (■) 275°C, and (◆) 310°C.

In Fig. 1 propane per batch volume is plotted logarithmically as a function of time for 0.81 wt% Pt/zirconia. Reaction isotherms measured at 230, 275, and 310°C are shown. The linearity of the data illustrates that propane oxidation, under our experimental conditions, can be described as first order in propane concentration. Increasing the oxygen pressure 2–5 fold had no effect on the oxidation rate. The system required about 10 min to reach steady-state conditions. In some cases, the rate decreased after about 90 min and the activity data deviated from linearity. However, the deactivation was reversible in that the original activity was completely restored after a brief evacuation at the reaction temperature between experimental runs. An example of reaction-isotherm curvature and its reproducibility is depicted in Fig. 2 for two consecutive activity experiments at 275°C for 0.81 wt% Pt/zirconia. The data presented in Figs. 1 and 2 for 0.81 wt% Pt/zirconia illustrate the limits in curvature, ranging from a good linear fit (Fig.

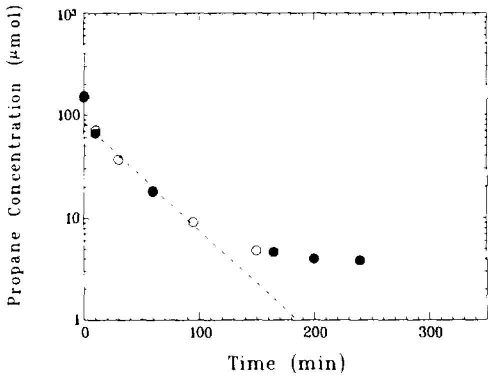

FIG. 2. Reaction isotherms of propane oxidation on 0.81 wt% Pt/zirconia at 275°C for (○) run 1 and (●) run 2.

1) to pronounced curvature (Fig. 2). No meaningful correlation between the occasional curvature and basic reaction parameters, such as Pt concentration or reaction temperature, was established. The reasons for the occasional deactivation remain uncertain and thus, the data were analyzed within the linear portion of the plot from 10 to 90 min.

The rate constant, k, can be described by two parameters k_0 and E. The preexponential factor, k_0, is related to the density of active sites and E is an apparent activation energy derived from the temperature dependence of k. The apparent activation energy remained constant at 17.8 ± 3.5 kcal/mol over the entire Pt concentration range, as shown in Fig. 3. Any systematic change with metal concentration, if it exists, falls within the limits of data scatter. This value is in agreement with previously reported activation energies for propane oxidation over Pt which range from 17 to 22 kcal/mol (*3–6*). Results of a parallel investigation (*5*) from this laboratory are also plotted in Fig. 3 for comparison. The average apparent activation energy obtained for Pt/γ-alumina (*5*), 22.1 ± 3.4 kcal/mol, is 4 kcal/mol higher than that over Pt/zirconia. At this point, the difference is thought to be insignificant considering the experimental uncertainty involved.

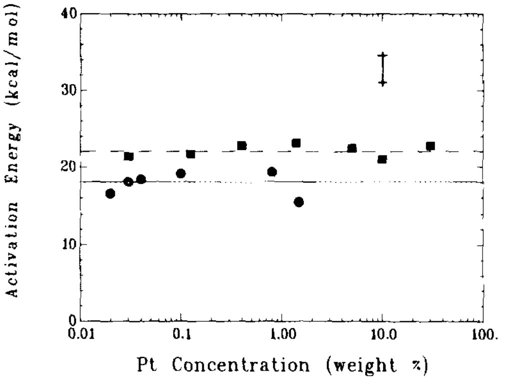

FIG. 3. Apparent activation energy for propane oxidation as a function of Pt concentration for (●) Pt/zirconia, (—) average for Pt/zirconia: 17.8 ± 3.5 kcal/mol; and (■) Pt/γ-alumina (*5*), (– –) average for Pt/γ-alumina: 22.1 ± 3.4 kcal/mol. Marker represents 3.5 kcal/mol.

Effect of Pt Concentration on Oxidation Rates

The dependence of the rate constant, k, on Pt concentration is shown in Fig. 4. The rate constant decreased by a factor of 20, from 152×10^{-3} to 6.55×10^{-3} min^{-1}, over the concentration range from 0.02 to 1.5 wt% Pt. Thus, for a given amount of Pt, the rate is fastest over highly dispersed metal and decreases as the particle size increases.

For highly dispersed Pt it is assumed that

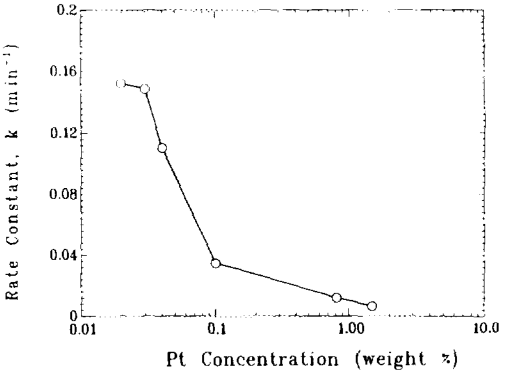

FIG. 4. Rate constant, k, for propane oxidation as a function of Pt concentration at 275°C. Values represent 4 mg bulk Pt for each case.

TABLE I

Dependence of Dispersion on Pt Concentration

Concentration Pt (wt%)	Measured Dispersion (CO : Pt = 0.70 : 1)	Assumed in Fig. 5
0.02	2.12	1.00
0.03	1.61	1.00
0.04	1.02	1.00
0.10	0.38	0.38
0.81	0.20	0.20
1.50	0.08	0.08

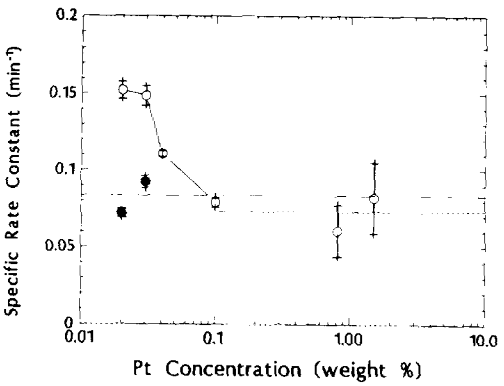

FIG. 5. Specific rate constant calculated per Pt surface atom for propane oxidation as a function of Pt concentration at 275°C. Values derived from dispersions listed in Table 1: (●) column 2, (– –) average value over concentration range: $82.6 \pm 17.3 \times 10^{-3}$ min^{-1}; (○) column 3, (–) average value above 0.10 wt% Pt: $72.9 \pm 10.9 \times 10^{-3}$ min^{-1}.

every Pt atom is a surface atom (*17*). As the concentration is increased and the particles begin to grow, the number of surface atoms on a constant amount of Pt decreases. An alternative approach is to express the rate constant per Pt surface atom. The dispersion, or fraction of surface atoms, was determined by CO chemisorption. Based on previous considerations (*5, 17*) an adsorption stoichiometry of $CO_{\text{chemisorbed}} : Pt_{\text{surface atom}} = 0.7 : 1$ was used to calculated metal dispersion. The measured dispersions are shown in the second column of Table 1. The tabulated values were corrected for CO adsorption on zirconia. Dispersion values in Table 1 for the two samples of lowest metal concentration, 0.02 and 0.03 wt%, exceed 1.0. A maximum value of one is expected for the dispersion when every Pt atom is a surface atom. For highly dispersed samples adsorption on the support can introduce a large error because of the extremely small amount of metal present. Also, multiple adsorption on highly dispersed metal cannot be ruled out (*7, 18, 19*).

An expression describing the turnover rate per Pt surface atom is derived by dividing the rate constant by the dispersion. This type of rate constant is examined in Fig. 5. Data reproducibility at the lower concentrations is quite good, as shown by the small error bars in Fig. 5. However, the calculation of a specific rate per surface Pt atom introduces another substantial intrinsic uncertainty associated with Pt dispersion. Based on CO adsorption (Table 1) dispersion values greater than unity were measured. It is questionable, however, whether multiple adsorption, which is indicated by the CO chemisorption data, exists also for the larger propane molecule, especially in the presence of oxygen. To illustrate this difficulty, two sets of data are plotted in Fig. 5 at the two lowest concentrations. The filled symbols display the specific rate constant calculated with the dispersion values measured by CO chemisorption (Table 1, column 2). The open circles represent the data assuming a maximum dispersion of one (Table 1, column 3). Clearly, an intrinsic shortcoming exists in determining a turnover rate per surface atom based on conventional chemisorption capacity. Indeed, one cannot always expect the basic assumption to hold that the density of chemisorption sites measured by one gas at room temperature represents the density of active sites involved in the catalytic reaction of another gas at a different temperature. Although frequently the reaction-site density appears to be proportional to a chemisorption-site density.

If a maximum dispersion of unity is assumed, the specific rate constant is greatest for the samples at the lowest concentrations and decreases by a factor of two to a constant value of $72.9 \pm 10.9 \times 10^{-3}$ min^{-1} above 0.10 wt% Pt (Fig. 5, solid line). This curve resembles the trend shown in Fig. 4 for the rate constant measured over a constant amount (4 mg) of bulk Pt. The change in Fig. 5, however, is quantitatively much less pronounced. An increased activity derived for the highly dispersed Pt has to be explained by an increase in the density of active sites, since the apparent activation energy remains constant with metal concentration. Somorjai (*20*) has pointed out that "rough surfaces do chemistry" presumably, at least in part, because of a more advantageous adsorption geometry. Surface roughness seems to prevail on smaller crystallites which tend to possess more kink and step sites and thus favor catalysis, while larger particles exhibit more planar or terrace sites (*10*). One cannot categorically reject a second interpretation of the data invoking a promotion effect of the zirconia support. However, it appears less likely that zirconia, which does not interact strongly with the active metal (*14*), would synergistically enhance the catalytic activity of Pt.

On the other hand, if a Pt atom would provide dual adsorption sites for propane the change in catalytic activity as a function of dispersion, i.e., particle size, becomes too small to be convincing within the reproducibility of the rate constant. Under the assumption of dual site adsorption, indicated by the filled symbols in Fig. 5, and considering the poor rate reproducibility at the two highest Pt concentrations the rate constant is given by a constant value of $82.6 \pm 17.3 \times 10^{-3}$ min^{-1} (Fig. 5, dashed line). Therefore, it can only be safely stated that different from γ-alumina which interacts strongly with highly dispersed Pt and deactivates it, zirconia does not inhibit the catalytic activity of Pt. In summary, the combination of a support that does not strongly interact with the metal and the abundance of certain Pt sites predominant on small clusters provides catalytic activity for propane oxidation which is as good as, if not better than that provided by larger Pt particles, where a support effect is negligible.

Effect of Sample Pretreatment

Redispersion of Pt on γ-alumina has been shown to occur under oxidizing conditions at about 500°C provided chloride was present (*17, 21–25*). The mechanism is thought to occur via a mobile platinum oxychloride species (*22, 24, 25*). The Pt/zirconia samples of this study were prepared from chloroplatinic acid and it was of interest to investigate whether platinum could be redispersed on zirconia as well.

Previously, CO adsorption was used to monitor changes in dispersion of Pt/γ-alumina after various pretreatments (*25*). In an analogous fashion, CO chemisorption was used to measure the dispersion of 0.10 wt% Pt/zirconia before and after exposure to oxygen. Evidence for Pt redispersion on γ-alumina under these conditions was observed after 12 h (*17*). After standard pretreatment the measured dispersion of 0.10 wt% Pt/zirconia was 0.38 ± 0.05. After exposure to oxygen for 96 h at 500°C the measured dispersion was 0.40 ± 0.04. Thus, Pt is not easily redispersed on zirconia compared to γ-alumina. Recall that zirconia does not interact strongly with the active metal compared to γ-alumina (*14*). Therefore, there is no driving force toward redispersion of Pt supported on zirconia as there is for γ-alumina.

To further investigate the effect of oxygen pretreatment on Pt/zirconia, experiments involving oxidation/reduction cycles at 500°C were conducted. Figure 6 is a plot of the rate constant over 4 mg of bulk Pt for a number of reaction isotherms. The data points represent the activity measurements at 230°C for 0.10 wt% Pt/zirconia. Points not shown (runs 3,5,6,7) were measured at 275°C. The vertical lines on the graph indicate the conditions of sample treatment prior to the activity experiment. The rate constant for the first three isotherms (runs 1,2,4) was $1.80 \pm 0.6 \times 10^{-3}$ min^{-1}. The sample was then

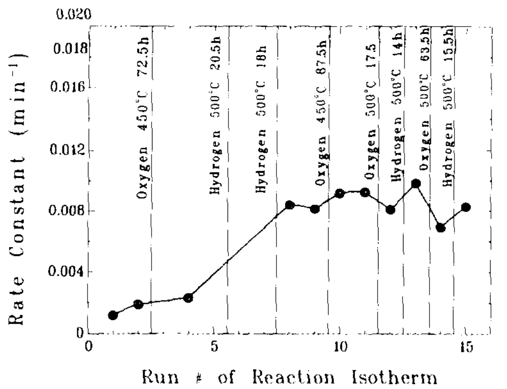

FIG. 6. Changes in rate constant, k, at 230°C after oxygen and hydrogen treatments at different temperatures and exposure times on 0.10 wt% Pt/zirconia.

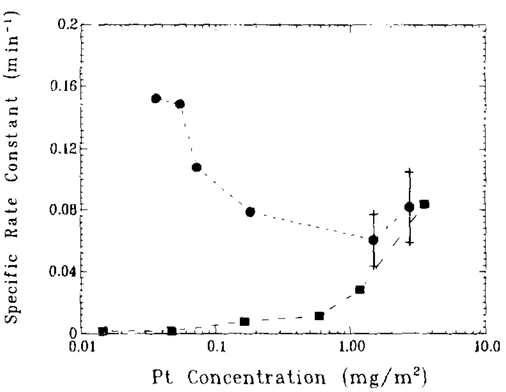

FIG. 7. Specific rate constant calculated per Pt surface atom for propane oxidation as a function of Pt concentration at 275°C for (●) Pt/zirconia and (■) Pt/γ-alumina (5).

heated in hydrogen at 500°C for 40 h. The propane activity increased 4.5 times to 8.42×10^{-3} min^{-1} (run 8). The sample was then alternatively heated in oxygen and hydrogen, mostly at 500°C, as shown in Fig. 6, with activity experiments at 230°C conducted between sample treatments. Overall, the rate constant remained unchanged at $8.52 \pm 0.9 \times 10^{-3}$ min^{-1} with further cycling. It is interesting to note that the catalyst sample appears to exist in two different "stable states." The first one of lower activity exists after standard sample pretreatment: calcination in air at 600°C for 20 h, followed by reduction in hydrogen at 400°C for 2 h and finally exposure to oxygen at 500°C for 20 h. Reduction in hydrogen at 500°C for 40 h produced a catalyst with significantly enhanced activity. Further exposure at 500°C to either oxygen or hydrogen had little effect on the propane oxidation rate. The lower initial activity may reflect an inhibition by residual chloride, which is removed during hydrogen treatment.

Comparison of Pt/γ-Alumina and Pt/Zirconia

To assess differences originating from the support, zirconia was chosen for a comparison with γ-alumina (5) since the two materials possess distinctly different properties. For example, zirconia is a highly crystalline material with a relatively low BET surface area of 5.5 m^2/g, compared to γ-alumina, which is poorly crystalline and has a much higher BET surface area of 85 m^2/g.

Figure 7 is a comparison plot of the dependence of the specific rate constant on platinum concentration for Pt/zirconia and Pt/γ-alumina (5) at 275°C. To account for the difference in support surface area the abscissa unit is a metal concentration term defined as the amount of Pt per BET surface area. For Pt/zirconia, the maximum specific activity for propane oxidation is found at low metal concentrations. At the same low concentrations, the specific activity for Pt/γ-alumina is at its lowest, two orders of magnitude less compared to Pt/zirconia. The difference in activity reflects the influence of the support on the catalytic metal. Small Pt particles supported on γ-alumina require a higher reduction temperature compared to large particles which behave similar to bulk Pt (*7*). This observation can be taken as evidence of the interaction between γ-alumina and highly dispersed Pt. Zirconia is a less reactive support compared to γ-alumina as indicated by infrared data of CO adsorption (*13*). Dispersed Pt on γ-alumina has a CO adsorption band at 2068 cm^{-1} and can be distinguished from crystalline Pt which has an adsorption band at 2080 cm^{-1}. For Pt/zirconia only one CO adsorption band at

2080 cm^{-2} was observed over the entire concentration range. This is evidence that Pt does not interact strongly with zirconia. Thus, it appears that highly dispersed Pt is very active for propane oxidation provided the metal is supported on an inert material. An alternative explanation, based on a synergistic catalytic enhancement of Pt by a weakly interacting zirconia, cannot be ruled out. On the other hand, small Pt clusters are partially deactivated when supported on γ-alumina because of an interaction with the support. Theoretical sites densities based on common reaction mechanisms can be calculated from fundamental constants and experimental data (*26*). Based on previous data (*5*), only one-third of the sites of highly dispersed Pt on γ-alumina are active for propane oxidation compared to highly dispersed Pt on zirconia. At higher Pt concentrations the influence of the support vanishes and the rate constants on both supports are the same, within experimental uncertainty, as expected.

Sample pretreatment can also have an influence on propane oxidation activity over Pt/zirconia and Pt/γ-alumina (*5*). Exposure to hydrogen at temperatures of at least 500°C increases the oxidation rate over both supports. While exposure to oxygen at 500°C has no effect on the rate for Pt on zirconia, redispersion occurs readily on γ-alumina (*17, 21–25*). In fact, a decrease in oxidation rate over Pt/γ-alumina has been observed even at temperatures below 300°C during propane oxidation (*5*).

CONCLUSIONS

(1) The specific rate of propane oxidation over Pt/zirconia calculated per Pt surface atom was found to decrease with Pt loading in the concentration range from 0.02 to about 0.10 wt% Pt (0.2–0.9 μmol Pt/m^2 BET surface area). This conclusion is based on the assumption that the oxidation process does not involve chemisorption of more than one propane molecule per Pt surface atom. Taking into account uncertainties associated with the apparent Pt dispersion it can be safely stated that the propane oxidation activity over Pt/zirconia is not lowered by a metal-support interaction. For higher concentrations, i.e., larger Pt particle size, the specific oxidation rate remains constant with Pt loading and is in agreement with that measured for Pt/γ-alumina.

(2) The catalytic activity of highly dispersed platinum for propane oxidation is at least one order of magnitude higher on Pt/zirconia than on Pt/γ-alumina. This observation is in agreement with results reported recently by Hicks et al. for methane oxidation (*13*). Thus, while Pt becomes deactivated by an interaction with γ-alumina, any interaction between platinum and zirconia, if it exists, results in catalyst promotion, not inhibition as is observed for Pt/γ-alumina.

(3) The rate change with particle size is predominately associated with a change in the density of active sites, since the apparent activation energy remains constant at 17.8 ± 3.5 kcal/mol with concentration. The average apparent activation energy for propane oxidation is somewhat lower than that measured for Pt/γ-alumina, but both values are considered to be identical within the experimental error.

(4) The lack of interaction between Pt and zirconia prevents redispersion of Pt, observed in the case of γ-alumina at low Pt concentrations. Thus, pretreatment in oxygen up to 600°C has been found to have little effect, if any, on the activity of Pt/zirconia.

ACKNOWLEDGMENTS

The authors thank Dr. R. W. McCabe for reviewing the manuscript and Dr. M. Shelef for his useful comments and suggestions.

REFERENCES

1. Germain, J. E., "Catalytic Conversion of Hydrocarbons," p. 240. Academic Press, New York, 1969.

2. Sigsby, J. E., Jr., Tejada, S., and Ray, W., *Environ. Sci. Technol.* **21**(5), 466 (1987).

3. Hiam, L., Wise, H., and Chaikin, S., *J. Catal.* **10**, 272 (1968).

4. Moro-oka, Y., Morikawa, Y., and Ozaki, A., *J. Catal.* **7**, 23 (1967).

5. Otto, K., Andino, J. M., and Parks, C. L., *J. Catal.* **131**, 243 (1991).

6. Yao, Y.-F. Y., *Ind. Eng. Chem. Prod. Res. Dev.* **19,** 293 (1980).
7. Yao, H. C., Sieg, M., and Plummer, H. K., Jr., *J. Catal.* **59,** 365 (1979).
8. Shyu, J. Z., and Otto, K., *Appl. Surf. Sci.* **32,** 246 (1988).
9. Otto, K., Weber, W. H., Graham, G. W., and Shyu, J. Z., *Appl. Surf. Sci.* **37,** 250 (1989).
10. Stevenson, S. A., Dumesic, J. A., Baker, R. T. K., and Ruckenstein, E., "Metal-Support Interactions in Catalysis, Sintering, and Redispersion," p. 142. Van Nostrand-Reinhold, New York, 1987.
11. Whetten, R. L., and Schriver, K. E., "Atomic Clusters in the Gas Phase," Department of Chemistry and Biochemistry, University of California, Los Angeles, CA, Jan. 1988.
12. Cox, D. M., Zakin, M. R., and Kaldor, A., *in* "Physics and Chemistry of Small Clusters," (P. Jana, B. K. Rao, and S. N. Khanna, Eds.), NATO ASJ Series C: Physics, Vol. 158, p. 741. Plenum, New York, 1987.
13. Hicks, R. F., Qi, H., Young, M. L., and Lee, R. G., *J. Catal.* **122,** 280 (1990).
14. Mercera, P. D. L., Doctoral Thesis, "Zirconia as a Support for Catalysts: Preparation, Characterization and Properties," p. 62. University of Twente, The Netherlands, June 1991.
15. Product Information Sheet, Aldrich Chemical Company, P. O. Box 355, Milwaukee, WI 1991.
16. Otto, K., Shelef, M., and Kummer, J. T., *J. Phys. Chem.* **74** (13), 2690 (1970).
17. Otto, K., *Langmuir* **5,** 1364 (1989).
18. Rabo, J. A., Schomaker, V., and Pickert, P. E., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964" Vol. II, p. 1264. Wiley, New York 1965.
19. Zaidman, N. M., Dzisko, V. A., Karnaukhov, A. P., Krasilenko, N. P., Koroleva, N. G., and Vishnyakova, G. P., *Kinet. Katal.* **9,** 863 (1968).
20. Somorjai, G. A., *Langmuir* **7** (12), 3176 (1991).
21. Plummer, H. K., Jr., and Otto, K., *in* "Proceedings, 47th Annual Meeting of the Electron Microscopy Society of America, San Francisco, CA, 1989."
22. Lieske, H., Lietz, G., Spindler, H., and Völter, J., *J. Catal.* **81,** 8 (1983).
23. Rickard, J. M., Genovese, L., Moata, A., and Nitsche, S., *J. Catal.* **121,** 141 (1990).
24. Anderson, J. A., Mordente, M. G. V., and Rochester, C. H., *J. Chem. Soc. Faraday Trans. 1* **85**(9), 2983 (1989).
25. Mordente, M. G. V., and Rochester, C. H., *J. Chem. Soc. Faraday Trans 1* **85** (10), 3495 (1989).
26. Maatman, R. W., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 29, p. 97. Academic Press, New York, 1980.