

Role of Metallic and Oxidic Platinum in the Catalytic Combustion of *n*-Heptane

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The total oxidation of *n*-heptane in oxygen and in air on Pt/Al₂O₃ has been studied with respect to pretreatment and reaction conditions. Calcination of the samples between 500 and 900°C does not decrease the activity, although the dispersion is dramatically diminished. Added chloride mainly deactivates dispersed samples. The catalysts are more active in air than in oxygen. Under certain conditions a pronounced oscillatory behavior of the oxidation is observed. The results can be explained by a dual-site model: active metallic Pt competes in the combustion with the less active oxidic surface complex [Pt^{IV}]_s. © 1987 Academic Press, Inc.

INTRODUCTION

Supported Pt catalysts are extensively used in hydrocarbon reactions, in conversions and in total oxidations. Extremely high dispersions with crystallites of 1 to 2 nm are prepared, for example, in reforming catalysts. Recently it was shown that highly dispersed Pt can easily be oxidized forming several distinct surface complexes with tetravalent platinum (1, 2). It is an interesting question whether this oxidized Pt favors or inhibits the catalytic oxidation. There are hints in the literature that the latter might be the case. Ostermaier *et al.* (3) investigated the oxidation of NH₃ and found a deactivation caused by oxidation of platinum. However, Niwa *et al.* (4) explicitly stated that in the oxidation of CH₄ supported Pt is completely oxidized.

Moreover, a periodic formation and decomposition of an oxidic overlayer has been proposed as a mechanism for the oscillatory behavior of catalysts (5-9). Such oscillations have recently attracted much interest (10-13). They are observed in oxidation reactions on Pt and on several other metal catalysts, mainly in the oxidation of CO (5-7, 9, 14-17) and of hydrogen (5, 18). Oscillations during hydrocarbon oxidations are scarcely known (19-23).

To sum up, the literature shows that some catalytic role of oxidized platinum has often been taken into account, but it is still uncertain whether it is a promoting or inhibiting role. The aim of the present work was to alter the oxidation state of platinum by different pretreatments and reaction conditions and to determine the influence on the combustion of *n*-heptane.

Experimental

Two types of Pt/Al₂O₃ catalyst, chloride containing (Pt_C) and chloride free (Pt), were prepared by impregnation of γ -Al₂O₃ with H₂PtCl₆ in aqueous HCl, and with H₂Pt(OH)₆ in aqueous HNO₃, respectively. Details of the procedures have been published previously (1). (Pt_C) contained 0.5 wt% Pt, (Pt) contained 0.1 or 0.5 wt% Pt. As a measure of Pt dispersion the hydrogen adsorption on the reduced sample was determined at 0°C, using a pulse technique (1).

For the total oxidation of *n*-heptane a continuous flow system was used with a vertical glass tube of 1 cm internal diameter as reactor, the catalyst being located on a frit. The amount of catalyst (0.3-0.8 mm diameter) was normally 0.1 g, diluted with 0.3 g α -Al₂O₃. The temperature was determined by a thermocouple contained in a glass tube immersed in the catalyst. A flow of

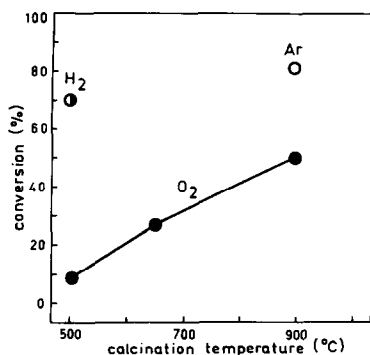


FIG. 1. Total oxidation (% conversion) of *n*-heptane at 195°C on (Pt_{Cl}) as a function of calcination temperature. Pretreatment in oxygen (●), hydrogen (○), or Ar (○).

oxygen or air (normally 2.26 liters/h) was saturated with 10 Torr *n*-heptane. The conversion was determined by gas chromatography. The procedure of testing was the following: heating to 350°C in oxygen or air, respectively, starting the reaction by admixing *n*-heptane and then decreasing the temperature in steps of about 10°C, determining the conversion at each step after 20 min, and after reaching the lowest temperature, heating up, step by step, again. As a result, activity/temperature curves of the typical S shape (23) were obtained. An example is shown later in the paper.

The methanation reaction of CO with H₂ was investigated in a microintegral reactor. The amount of catalyst used was 300 mg (0.2–0.6 mm diameter). The prerduced catalyst was heated to 350°C in a stream of hydrogen containing 1 vol% CO (3.6 liters/h) and then cooled to room temperature in the reaction gas at 2 K/min. The conversion of CO was determined by gas chromatography as a function of temperature.

RESULTS

Calcination Effects

The Pt catalysts, chloride-free as well as chloride-containing were calcined in the temperature range between 500 and 900°C. These catalysts were used in the oxidation of *n*-heptane.

The percentage of conversion as a function of the temperature of calcination in O₂ with catalyst (Pt_{Cl}) is plotted in Fig. 1. The only product is CO₂. Surprisingly, the conversion increases with increasing calcination temperature. Ar treatment is still more effective than O₂ calcination. Prereduction in hydrogen is also a means to activate the catalyst calcined at low temperature.

A corresponding diagram for the chloride-free catalyst is shown in Fig. 2. These samples were calcined in air. The calcination up to temperatures of 900°C has nearly no effect on the conversion. After the measurement the samples calcined at 500 and 1000°C, respectively, were impregnated with 0.5 N HCl, recalined at 550°C, and reexamined. Chloride poisons the combustion, but with remarkable differences. The sample precalcined at 500°C was heavily poisoned, whereas the other one remained nearly as active as before.

The influence of the calcination temperature on the Pt dispersion as characterized by the H/Pt adsorption ratio is seen in Fig. 3. The dispersion of the (Pt) sample is considerably lower than the dispersion of the (Pt_{Cl}) sample. As expected, the increased calcination temperature effects a strong decrease of the dispersion. Moreover, the thermal stabilities of the chloride-free samples are distinctly lower than those of the chloride-containing ones.

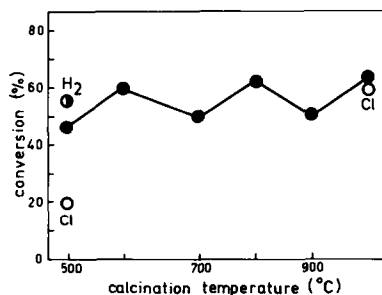


FIG. 2. Total oxidation (% conversion) of *n*-heptane at 230°C on (Pt) as a function of calcination temperature. Calcined in air (●), prerduced in hydrogen (○), after calcination impregnated with HCl (○).

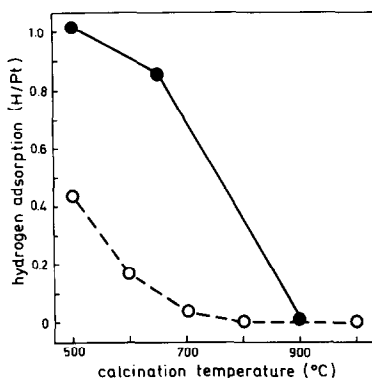


FIG. 3. Adsorption of hydrogen (H/Pt) on (Pt_{Cl}), calcined in oxygen (●), and on Pt, calcined in air (○), as a function of calcination temperature.

The activity of the calcined catalysts in a reducing atmosphere has been studied in the hydrogenation of CO to methane. The results are shown in Fig. 4. With increasing calcination temperature the conversion of CO dramatically decreases. The dispersion of Pt decreases, too, and a nearly linear relationship is seen, indicating a constant specific activity in spite of varying dispersion. This is in striking contrast to the heptane oxidation with a very low specific activity for the highly dispersed samples.

The influence of the ratio pO_2/pHC was tested by oxidation experiments in pure oxygen or in air, respectively, resulting in pO_2/pHC ratios of 75/1 and 15/1, respectively. The excess of oxygen in the oxygen-rich mixture was 6.8-fold and in the oxygen-lean mixture 1.36-fold, related to the stoichiometric mixture.

As an example (cf. Experimental), the whole curve of the always-measured activity/temperature dependence is plotted. The results are shown in Fig. 5. In pure oxygen a highly dispersed (Pt_{Cl}) catalyst, only calcined at 500°C in oxygen, displays a surprisingly low activity for the combustion (solid line with open circles). In air the same catalyst is much more active (dashed line). This implies that the lowering of the oxygen partial pressure increases the activity of oxidation. However, this effect de-

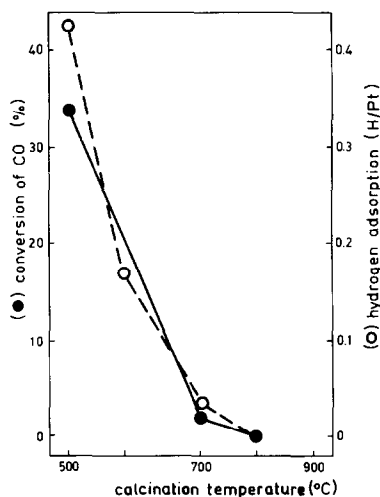


FIG. 4. Hydrogenation of CO to CH_4 (% conversion of CO) at 345°C on Pt (●) and dispersion (H/Pt) of the platinum (○) as a function of calcination temperature, calcined in air.

pends on the dispersion of the catalyst. A poorly dispersed catalyst, treated at 900°C in Ar, is already very active in oxygen (solid line with solid circles), and air has only a small promoting effect (dashed line). Taking the temperature of 50% conversion as a measure of activity, the corresponding lowerings of the temperatures with oxidation by air are 75°C on the dispersed and 25°C on the sintered sample.

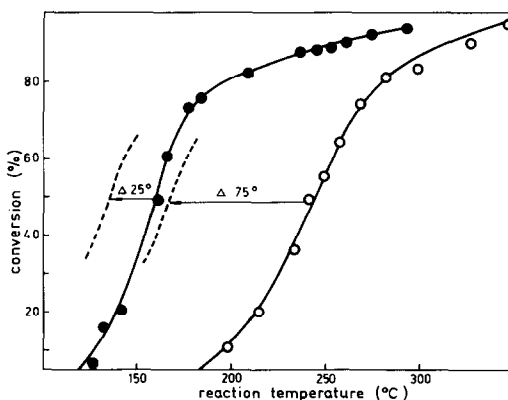


FIG. 5. Total oxidation of *n*-heptane (% conversion) on chloride-containing dispersed Pt (○) and sintered Pt (●) in oxygen (solid lines) and in air (dashed lines) as a function of reaction temperature.

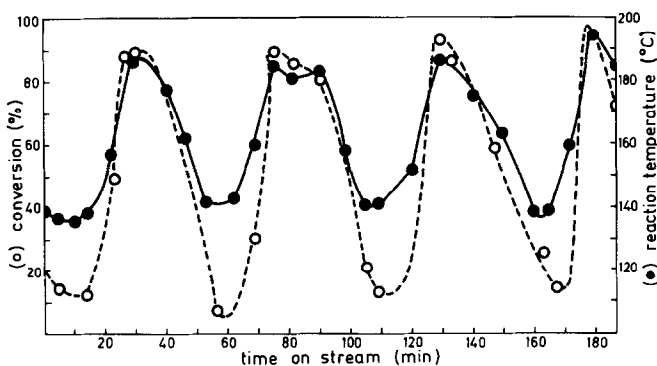


FIG. 6. Oscillatory behavior of *n*-heptane combustion in air on (Pt). Conversion (○) and reaction temperature (●) as a function of reaction time at constant temperature of the furnace (178°C).

Oscillatory Behavior

Under certain critical conditions very pronounced periodic oscillations of the combustion occurred. These data are depicted in Fig. 6. The frequency of the oscillation was about 0.8 h^{-1} . During one cycle the temperature in the catalyst bed varied between 140 and 190°C and the conversion between 10 and 95%. The temperature of the furnace was kept constant at 178°C . No significant change of the periodic oscillations could be observed within 200 min. The only product was CO_2 , especially checked at the minimum and at the maximum of the conversion.

The catalyst was (Pt) with 0.5 wt% Pt, calcined at 400°C in air. The reaction was started as usual by admixing heptane to the stream of air at 350°C . Then the temperature was lowered step by step until the oscillating regime was reached.

Special care is necessary for optimal conditions. The catalyst weight used was 180 mg, the space velocity 210 h^{-1} , and the ratio $p_{\text{O}_2}/p_{\text{HC}} = 15$. With 50 mg only a very slow recovery of the conversion after the typical decay occurred; with 400 mg the combustion always remained at 100%, even after switching off the external furnace. A corresponding behavior was observed by variation of the flow rate at constant catalyst weight of 100 mg, a flow rate of 1.13

liters/h (105 h^{-1}) being too low, and 4.40 liters/h (410 h^{-1}) too high.

With the other samples mentioned in this paper, only sometimes were slight hints of an unstable behavior observed.

DISCUSSION

High temperature calcination of the Pt catalysts causes an increased activity of the highly dispersed (Pt_{Cl}) samples but has almost no influence on the activity of the poorly dispersed (Pt) samples (Figs. 1 and 2).

The dispersion of both the catalysts decreases distinctly with increasing calcination temperature (Fig. 3). As found previously (1, 2), the highly dispersed Pt on alumina is transformed into an oxidized surface complex $[\text{Pt}^{\text{IV}}]_{\text{s}}$ by treatment in oxygen or air at 500°C . Treatments at higher temperatures cause a decomposition of the complex into poorly dispersed metallic, crystalline platinum (Pt_{cr}).

Taking this into account, a model with two different active sites is proposed. The combustion is catalyzed by $[\text{Pt}^{\text{IV}}]_{\text{s}}$, as well as by (Pt_{cr}), but the latter species is the much more active one. Hence the (Pt_{Cl}) sample, calcined at 500°C , contains only the less active species and therefore must be less active (Fig. 1). With increasing calcination temperature, increasing amounts of active (Pt_{cr}) are formed and the activity

increases. Treatment in Ar, being known to produce still more metallic platinum than oxygen treatment (24), should further increase the activity, as observed.

Surprisingly, prereduction in hydrogen at 500°C produces a very active catalyst, although a reoxidation is to be expected during the heating up before the start of the reaction. It may be that hydrogen treatment produces some large platinum crystals, which are resistant to reoxidation and are sufficient for a high activity.

The activity of the chloride-free sample proves to be nearly independent of the temperature of calcination (Fig. 2). This suggests that the number of active sites remains nearly constant. The initial dispersion of 0.45 after calcination at 500°C is relatively low (Fig. 3). This is a distinct hint of the existence of larger amounts of crystalline, active (Pt_{cr}), besides small amounts of dispersed $[Pt^{IV}]_s$. The transformation of the latter into (Pt_{cr}) by further thermal treatments should have only a limited influence on the total surface area of the (Pt_{cr}) and hence on the total activity.

On the other hand, the independence of the activity on thermal treatments could be suggestive of a heterogeneous-homogeneous reaction mechanism. It is known that combustions can be catalytically initiated (23). In this case a small amount of (Pt_{cr}), present in all the samples, would be sufficient for the combustion.

The observed unusual thermal stability of the Pt catalysts should be valid only in oxidizing reactions, because only under these conditions can the less active oxidic surface complex be formed. Hence a counter-experiment was made under reducing conditions, namely, CO was hydrogenated. As the results proved, under these conditions the same catalysts were thermally unstable and a normal decrease of activity with decreasing dispersion was observed (Fig. 4).

An unusual increase of activity with decreasing dispersion of Pt has also been observed in the oxidation of hydrogen (25) and of CO (26, 27). The specific activity of

very small crystallites has been found to be much lower than those of larger crystals.

The addition of HCl poisons the activity. However, only the dispersed, and not the sintered sample, is heavily poisoned (Fig. 2). It is known (1) that chloride enables a redispersion by transforming (Pt_{cr}) to $[Pt^{IV}]_s$; this process should proceed more easily with a more dispersed catalyst than with a sintered sample. Therefore the dispersed catalyst should be more sensitive to poisoning by chloride. This was observed.

Oxygen causes a further poisoning effect. The catalysts are less active during the combustion in oxygen than in air. Such a negative effect of oxygen is exceptional. Usually there is a positive influence of pO_2 or no influence at all on the combustion (28). This strange effect again becomes understandable, assuming different chemical states of Pt, now caused by different atmospheres. During the combustion in pure oxygen the atmosphere is a more oxidizing one; hence the highly dispersed Pt exists as the less active $[Pt^{IV}]_s$. However, during the combustion in air a reducing effect of heptane in the mixture becomes dominant and the oxidized platinum is reduced to active zerovalent platinum. Moreover, this effect should be more pronounced in dispersed catalysts, containing more $[Pt^{IV}]_s$, than in sintered catalysts. This has been observed.

A similar concept with a varying reducing effect can explain the observed oscillations. Basically, alternating formation and reduction of oxidic Pt is assumed. During the period of increasing conversion the exothermic combustion causes a self-heating of the sample. At maximum, a nearly complete conversion is achieved. This implies a nearly complete consumption of the reducing heptane. However, the excess of oxygen remains. In this oxidizing atmosphere active metallic Pt is transformed into less active oxidic Pt. The consequence is a drop in activity and hence in temperature. The conversion slows down. At the minimum, the partial pressure of the remaining heptane reaches a maximum and therefore the

reducing effect reaches a maximum, too. Now the less active $[\text{Pt}^{\text{IV}}]_s$ is reduced to active Pt_{cr} . The cycle starts again.

This proposed mechanism belongs to the widely examined kinetic models of periodically formed buffers in catalytic combustions (13). The chemical nature of the buffers is still a matter of controversial discussion. Postulated as buffers are adsorbed (5) or oxidic oxygen (6, 20–22, 29), adsorbed CO (14, 30), or CO_2 (15), and even a hydride (31). The present oscillation in the combustion of *n*-heptane is characterized by extremely large amplitudes of the rate and by extremely low frequencies of the oscillation. This may be caused by the proposed buffer, the slow formation, and decomposition of the $[\text{Pt}^{\text{IV}}]$ -alumina surface complex.

CONCLUSION

Several interesting effects have been observed during the combustion of *n*-heptane. The activity of Pt is not diminished by high temperature calcination, although the dispersion is drastically decreased. The activity is higher in air than in oxygen. A pronounced oscillatory behavior can be initiated. All these effects are explained by a dual-site model. Depending upon specific conditions the state of Pt alternates between less active oxidized Pt and highly active metallic Pt.

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