JOURNAL OF CATALYSIS **152**, 410–414 (1995)

NOTE

The Role of Chlorine in Induction Periods during the Oxidation of Methane over Pd/SiO_2[1]

Supported palladium catalysts are active for the methane oxidation reaction at temperatures above ca. 535 K (1–3):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \qquad [1]$$

When first exposed to reaction conditions Pd-based catalysts display activity that varies with time on stream. The nature of this transient activity varies; reported behaviors include (i) no activity followed by high activity that declines to a steady level, (ii) initial high activity that declines to a steady level, (iii) no activity followed by a slow increase in activity to a steady level, (iv) initial low activity that increases to a steady level, and (v) low initial activity that increases but fails to reach a steady level (within the time frame observed) (3–11). Given this variety of observations, it is not surprising that several explanations for the initial transient behavior of Pd-based catalysts have been offered, some of which are contradictory.

Several independent groups have reported that the rate of reaction increases with time on stream. Two groups have also compared catalysts prepared from two different precursor salts, specifically nitrates and chlorides. Cullis and Willatt (3), using a pulsed microreactor, reported that "the use of palladium II nitrate rather than tetraammine palladium chloride for the preparation of palladium catalysts had no appreciable influence on the subsequent activity." Baldwin and Burch (7) observed that the activity of catalysts (whether from nitrates or from chlorides) increased linearly with time on stream. They concluded that the catalyst precursor (residual chlorine) was not the cause for the transient behavior of the catalysts, but that it was the result of a morphological change (perhaps associated with the dissolution of carbon) that generated sites of higher activity.

In apparent contrast, Simone *et al.* (11) report that catalysts prepared from $Pd(NO_3)_2$ give "considerably better activity than $PdCl_2$." Here the catalysts were evaluated by continuous temperature ramping under reaction conditions to find the temperature at which a specified conversion (30%) was attained. For the catalysts prepared from the chloride they observed that catalysts previously conditioned at reaction conditions reached 30% conversion at lower temperatures than catalysts that were not so conditioned. In addition they found that a double washing procedure could be used to prepare catalysts from chlorides with significantly lower levels of residual chlorine, and this procedure also lowered the temperature at which the catalysts reached 30% conversion. They concluded that catalytic activity increases as the residual chlorine content is decreased.

Primet and co-workers (4, 5) made virtually the same observation: when catalysts (prepared from chlorides) were previously conditioned at reaction conditions, they became active at lower temperatures than catalysts that were not so conditioned. However, in this case they concluded that the reason for the increase in activity was a restructuring of the particles (including an increase in average particle size) leading to a weaker Pd–O bond, and consequently higher activity. Their procedure differed from that of Simone *et al.* in that instead of using a continuous temperature ramp at reaction conditions, they increased the temperature in discrete steps. At each step they observed that the rate of reaction increased with time on stream. This behavior was associated with the formation of bulk PdO since it was observed only in the composition range where bulk PdO formation is favored.

In one study, Hicks *et al.* (9) observed all five of the types of transient behavior previously listed, and in all cases the catalyst precursors contained chlorine. The primary focus of that work was on the final activity of the catalysts, not the transient behavior. The study concluded that the activity depends upon particle size; PdO that is highly dispersed on the support is less active than PdO that forms on the surface of large catalyst crystallites. There were catalysts, however, which did not conform to this classification. The authors also noted the possibility that residual chlorine from the catalyst precursors might affect activity.

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0021-9517/95 $6.00

In short, it is very well established that Pd-based catalysts catalysts exhibit transients in activity when first brought on stream in methane oxidation. It is also very well established that chlorine poisons Pd-based catalysts for this reaction (12–14). However, as the works just cited reflect, the importance and effects of *residual* chlorine left on the catalyst after its preparation are neither as clearly defined nor understood. This note makes two points relative to this issue. First, there are at least two essentially unrelated phenomena underlying the initial transient behavior of Pd-based catalysts when first exposed to methane oxidation conditions. Herein these phenomena will be called induction (a period of time while the catalyst is exposed to reaction conditions during which no catalytic activity is observed) and activation (while exposed to reaction conditions the catalyst's activity increases steadily with time). The second point of this note is that residual chlorine is the primary cause for induction, but it plays a negligible role with respect to activation.

In the present work silica-supported Pd has been employed. Catalysts were prepared from aqueous solutions of palladium chloride (Johnson Matthey Corporation) by impregnating silica gel (Grace high purity grade, 200 μm average particle size, 350 m^2/g) to incipient wetness at a nominal loading of 1 wt% palladium (as metal). An "unwashed" catalyst was prepared directly, and a "double washed" catalyst was prepared using the procedure described by Simone *et al.* (11) to generate a low residual chlorine level. Each of these catalysts was heated in air at 300°C for 3 hr and then reduced in 50 cm^3 (stp) min^{-1} pure hydrogen at 275°C and 1 atm to complete their preparation. Catalyst chlorine content was measured potentiometrically using a selective chloride ion probe (Orion Research EA 940) by digesting samples in 13 *M* HNO_3. TEM and chemisorption measurements indicated an average particle size of ca. 10 nm.

Ultra-high purity grade (99.999%, <3 ppm moisture) hydrogen (Linde), a high purity grade mixture (±2% of key component) of 0.5% oxygen in helium (Linde), and ultra-high purity grade (99.97%, <10 ppm moisture) methane (Linde) were all used without additional purification. High purity grade (99.995%, <5% moisture) helium (Linde) was additionally treated using a Supelco carrier gas purifier followed by a LabClear adsorbent bed before its use as the carrier gas for the gas chromatograph and as the reactor purge gas.

Catalyst activity was measured in a ¼ in. stainless steel, fixed bed, microreactor operating at 548 K and atmospheric pressure using 400 (±15) mg of catalyst per run. Reactant and product gases were analyzed using either a Varian 1400 gas chromatograph with a thermal conductivity detector or a UTI (Model 100C) quadrupole mass spectrometer. The reactor feed, 105 cm^3 (stp) min^{-1}, in all cases was rich in methane (approximately 5% methane, 0.5% oxygen, balance helium). Under these conditions the conversion of oxygen was less than 100%. "Partial oxidation" products like CO and H_2 are not expected to appear as products before all the oxygen is consumed. Hence CO_2 and H_2O were the only products, allowing the conversion of oxygen to be used as a measure of catalytic activity. In blank runs with an empty reactor and with neat silica gel, no activity was measured at these conditions.

Figure 1 shows the oxygen conversion as a function of time on stream for the unwashed catalyst, for the double washed catalyst, and for the unwashed catalyst after it had previously been exposed to reaction conditions and then reduced again. The unwashed catalyst shows an induction period of approximately 120 min, while the double washed catalyst shows an induction period of around 20 min. The previously used catalyst does not show induction behavior. Table 1 shows the chlorine levels of the catalysts at various points in the experimental process. It is clear that both the washing process (compare as-prepared unwashed and double washed) and reaction conditions (after pretreatment and after reaction) lead to a reduction in the chlorine level.

A careful examination of the results shows that the reused catalyst does not show an induction period, and its chlorine level is 0.804 mg Cl/g catalyst. The twice-washed catalyst has a slightly higher chlorine level (0.85 mg/g), and it does display a brief induction period. The difference in induction period between these two cases might be attributable to the small difference in chlorine level, or it might be primarily attributable to differences in the distribution of chlorine on the catalysts (on the metal vs on the support near the metal vs on the support

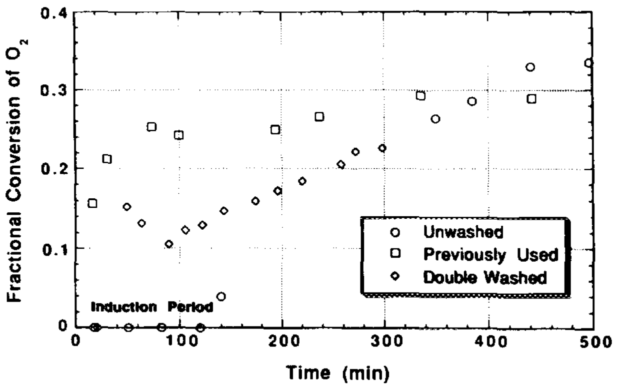

FIG. 1. Activity of Pd/SiO_2 catalysts prepared from chlorides as a function of time on stream under methane oxidation conditions. An unwashed catalyst (circles) displays no activity for the first 120 min on stream; a double washed catalyst (diamonds) becomes active after only 20 min, and a catalyst that has previously been exposed to reaction conditions (squares) is active as soon as it is brought on stream.

TABLE 1

Chlorine Content after Various Treatments

Sample condition	Unwashed (mg Cl/g catalyst)	Double washed (mg Cl/g catalyst)
As prepared	9.08	0.85
Reduced but not exposed to reaction	1.8	0.5
Reduction and exposed to reaction	0.804	0.450

far from the metal—see below). The present results do not allow a choice between these possibilities, but they do show clear correlation between lower chlorine levels and shorter induction periods. It is interesting to note that reaction conditions cause a further decrease in the chlorine level of the washed catalyst, suggesting that reaction conditions may be more effective than washing for the removal of some forms of catalyst chlorine.

The gas phase was monitored during the induction period using a mass spectrometer. In addition to the expected reactant and product mass fragments, a broad signal (spanning ca. 4 amu) was observed; its maximum intensity was at 134.8 amu. The poor resolution of this fragment makes a definitive assignment difficult, but it is believed to be a fragment from trichloromethanol. The mass spectrometer signal intensity at *m*/*e* = 134.8 was measured as a function of time on stream using both the unwashed and the double washed catalysts and is shown in Fig. 2. The figure also indicates the time at which catalytic activity for methane oxidation was first observable. Both catalysts that displayed an induction period evolved this species during that period, the length of time during which this species evolved from each catalyst is equivalent to the induction period for that catalyst, and both catalysts began to exhibit catalytic activity when this species stopped evolving. Considering the concomitant decrease in chlorine level of the catalysts when exposed to reaction conditions, we believe that this species is generated by the reaction of methane and oxygen with residual chlorine on the catalyst to form trichloromethanol which desorbs, thereby removing residual chlorine.

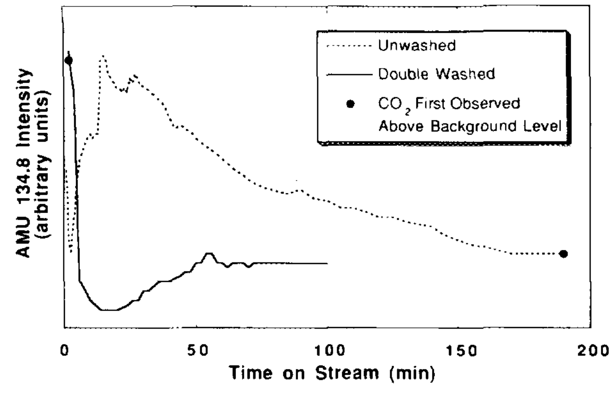

FIG. 2. Intensity of the mass spectrometer signal corresponding to atomic mass 134.8 immediately after the Pd/SiO$_2$ catalysts prepared from chlorides are exposed to reaction conditions. The broken line represents an unwashed catalyst and the solid line represents a double washed catalyst. The circle on each trace shows the time when the catalyst first became active as evidenced by the detection of CO$_2$ above background levels.

The data just presented are totally consistent with the hypothesis that the induction period is directly caused by residual chlorine from the catalyst preparation and that once such chlorine is removed the catalyst will no longer display induction. Indeed, we have reused many, many catalysts and have never observed induction behavior, and conversely the only time we have observed induction behavior is with freshly prepared catalyst. On the other hand, the catalyst activation phenomenon (steadily increasing catalytic activity with time on stream) has been observed with virtually every catalyst we have studied, regardless of whether is has been exposed to reaction conditions or not.

Table 1 indicates that even after use the catalysts retain a finite amount of chlorine. This raises the possibility that the activation phenomenon (steadily increasing catalytic activity with time on stream) could also be due to the slow removal of chlorine. If this is true, then once a catalyst has been activated to a given level, its activity should not drop back below that level because the chlorine is permanently removed. The experimental results presented in Fig. 3 show that each time the same catalyst is reduced in pure hydrogen at 275°C and subsequently put back under reaction conditions, its initial activity drops to a low level and then again increases steadily with time on stream. This is convincing evidence that the

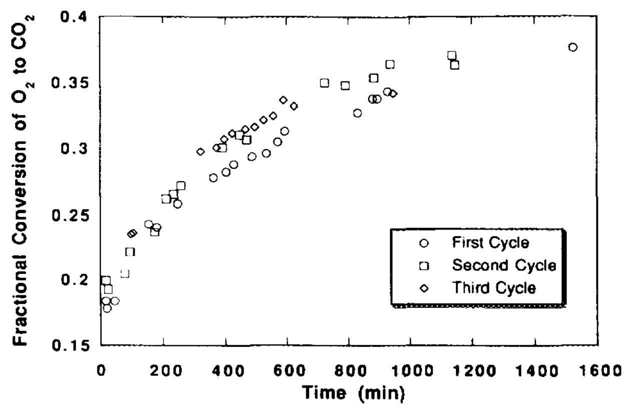

FIG. 3. Conversion of oxygen as a function of time on stream during three back-to-back cycles of reduction in hydrogen followed by exposure to reaction conditions.

activation phenomenon is not caused by slow removal of residual chlorine; no chlorine was added back to the catalyst between the end of one cycle and the start of the next.

Furthermore, if the catalysts was pretreated in 0.5% oxygen instead of being reduced, activation behavior was also observed. This argues against the possibility that chlorine moving from the support to the metal causes activation. For this to be true, the chlorine would have to migrate during both hydrogen reduction and mild oxidation pretreatments, but not during methane oxidation. As already noted, activation (but to our knowledge not induction) has also been reported for catalysts prepared from nitrates.

Apparently chlorine below a certain threshold level has little effect upon the activation phenomenon. There are similar reports in the literature for other systems. The rate of isotopic exchange of oxygen on supported Pt is not affected by the presence of chlorine at levels below ca. 0.2%, while higher catalyst chlorine contents result in a decrease in the rate of isotope exchange (15). XPS studies on supported Pt catalysts indicate two kinds of chlorine; one is associated with the metal and can be easily removed, while the other is associated with the support and is difficult to remove (16). A distinction between chlorine associated with metal and with support has also been noted for supported Ru (17). Chlorine on the support but far from the metal particles would not be expected to affect the activity of the metal particles.

The two points made here, namely that there are two types of transient behavior (induction and activation) and that only one of them is attributable to residual chlorine (induction), are easily reconciled with the literature reports cited earlier. The two reports that concluded catalysts prepared from nitrates and from chlorides are equivalent never detected an induction period, only activation (3, 7). Apparently the details of their preparative procedure or catalyst pretreatment resulted in a fresh catalyst with a low enough residual chlorine level so that induction did not occur. The activation phenomenon which they did observe is not caused by residual chlorine, and consequently it is immaterial whether nitrate or chloride precursors were employed.

Simone *et al.* (11) used a continuous temperature programming technique to assess catalytic activity. When a fresh catalyst is experiencing induction, the temperature continues to rise and consequently 30% conversion is not reached until a relatively high temperature. Upon conditioning at reaction conditions or double washing, the data in Table 1 and Fig. 1 indicate that residual chlorine levels are reduced to below the level where induction occurs. In continuous temperature programming of such a catalyst, 30% conversion will be reached at lower temperatures. It is important to note that even though the temperature for 30% conversion is considerably lowered, this does not mean that the other phenomenon, namely activation, is not taking place. Indeed, the work of Primet and coworkers (4, 5), using temperature programming in discrete steps, shows that activation is occurring, even on the conditioned (reduced chlorine level) catalysts. The conditioned catalyst displayed activation at each discrete temperature step.

In conclusion, the transient behavior of Pd-based catalysts upon first exposure to methane oxidation conditions should not be attributed to a single cause. There are at least two distinct processes taking place, induction and activation. The induction behavior can be directly related to the level of residual chlorine on the catalyst. The present results do not indicate the cause for the activation phenomenon; there may be multiple causes. Some possibilities include catalyst restructuring, catalyst redispersion under reaction conditions, and a change in catalyst oxidation state under reaction conditions. The present results do, however, indicate that the slow removal of residual chlorine from the catalyst is not the cause of activation.

ACKNOWLEDGMENTS

This material is based upon work supported partially by the National Science Foundation under Grant CBT-8857100. The authors also gratefully acknowledge partial support of this research by Johnson Matthey, Ltd., who also provided the palladium.

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Received April 8, 1994; revised November 16, 1994

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