EXAFS Studies of the Poisoning Effect of Cl on Pt/Al_2O_3 Catalysts during Oxidation Reactions

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Introduction

The complete combustion of methane by Pt and Pd catalysts has been studied in relation to pollution control of emissions from natural gas vehicles (NGV),[1] as well as for the oxidation of methane in turbines for power generation.[2] Supported Pt catalysts are often prepared from Cl-containing precursors such as H_2PtCl_6, and it has been reported that Cl poisons the oxidation activity.[3-5] The state of the active catalyst's surface and the effect of Cl poisoning on the activity, however, have not been elucidated.

Liebske et al.[6] were among the first to propose a model of the various phases that could be present as a function of pretreatment conditions in a Pt/Al_2O_3 catalyst prepared from Cl precursors. These phases, however, were not correlated with the catalyst's activity. Based on temperature-programmed reduction of Pt catalysts oxidized at different temperatures, Hwang and Yeh[7] concluded that four types of oxide species could be formed. These authors proposed that at room temperature, there is a surface oxide, $PtO_{0.7}$. At 100°C, PtO is formed, while at 300°C, Pt further oxidized to PtO_2. Oxidation at 600°C leads to metallic Pt and platinum aluminate. In addition, preparation of the catalyst from a $PtCl^4$ precursor results in a PtO_xCl_y complex, which can be removed by reduction in H_2 at 400°C.[3] In a similar study, Burch and Loader[8] concluded that the oxidation activity of Pt catalysts was optimal for a partially oxidized and reduced surface.

We have used EXAFS to determine the structure of the active Pt species for methane oxidation and to characterize the state of the surface on Cl-free and Cl-containing Pt/alumina catalysts. In related work, we have studied H_2 and CO chemisorption, O_2 isotopic exchange, and the reaction kinetics. At low methane concentration (0.3 vol.% CH_4, 16 vol.% O_2) the Cl-free catalyst was about 20 times more active during complete methane oxidation than the Cl-containing catalyst. However, the activity of the Cl-free catalyst was strongly dependent on the reactant concentration. Exposure of the Cl-free catalyst to higher concentrations of methane (3 vol.% CH_4) reduced the activity to a level similar to that of the Cl-containing catalyst. Addition of HCl to the Cl-free catalyst rendered the activity identical to the catalyst prepared from Cl-containing precursors.

Materials and Methods

Two samples were prepared, both with 1.5 wt.% Pt on Al_2O_3, one with Cl and one Cl-free. EXAFS data were collected at room temperature for the calcined, reduced, and oxidized catalysts.

Results and Discussion

Calcination of Pt catalysts leads to Pt(IV) with 6 nearest neighbors: 6 Pt–O bonds in the Cl-free catalyst, but 2.5 Pt–Cl and 3.5 Pt–O bonds in the Cl-containing sample. No Pt–Pt bonds are observed in the calcined catalysts. The Pt–O bond distance of about 2.06 Å is characteristic of a Pt(IV)-oxide bond, and the Pt-Cl distance of 2.31 Å is, within experimental error, identical to that in H_2PtCl_6.[9]

Reaction at 300°C in H_2 results in complete reduction to small metallic Pt particles. A fully coordinated shell in Pt metal consists of 12 nearest-neighbor Pt atoms. The coordination numbers of 6.6 and 6.9 Pt neighbors for the two catalysts show that, on average, the first shell of every Pt atom is not completely coordinated to Pt. This finding indicates small metallic Pt particles. Assuming that the geometry is compact and that the Debye-Waller factor has been modeled correctly, the average particle diameter is 9 ± 3 Å. These values are consistent with the H_2 chemisorption results, indicating that the dispersions are ~0.8. The signal of reduced Pt particles is sufficiently small that there is a contribution to the EXAFS from the oxygen ions of the support. The Pt–O distance of 2.20 ± 0.02 Å is similar to that previously reported for Pt, Rh, and Ir catalysts.[10]

Reaction at 300°C in 5% O_2 (balance He) indicates a more complicated environment. The remainder of a small Pt-Pt contribution to the EXAFS at a distance of 2.7 Å indicates that the small metallic particles are not fully oxidized under these conditions. The Pt-Pt coordination numbers were 3.6 for the Cl-free sample and 0.9 for the Cl-containing sample. The Cl-free catalyst has 3.9 Pt–O bonds, while the Cl-containing catalyst has 2.0 Pt–O and 2.5 Pt–Cl bonds. Identical results were obtained for the oxidized catalysts treated with 5% O_2 alone, 0.3% CH_4 and 16% O_2, or 3% CH_4 and 16% O_2 at both 300°C and 450°C. Finally, after oxidation, both catalysts were re-reduced in H_2 at 300°C. The results were identical to those obtained prior to oxidation. This finding indicates no sintering of the Pt during oxidation.

After oxidation at 300°C, the Cl-free catalyst still has exposed, reduced Pt atoms at the particle surface, which chemisorb CO, undergo oxygen isotopic exchange, and are active for methane oxidation. These results suggest that the active site is metallic Pt. This model agrees well with that proposed by Burch and Loader,[8] who concluded that neither a fully reduced nor a fully oxidized surface is optimal for methane oxidation. While oxidized Pt/alumina with Cl also has a metallic core — possibly as small as two Pt atoms — the surface contains both Pt–O and Pt–Cl bonds. Since no Pt–Cl bonds occur in the reduced catalyst, it is likely that the Cl bound to the alumina support migrates to the Pt particles during oxidation. The inability of this catalyst to adsorb CO or induce O_2 isotopic exchange suggests that no reduced Pt atoms appear on the surface. The low methane oxidation activity is likely due to the nearly complete coverage of the surface by Cl (and O). The mechanism of chloride poisoning, therefore, appears to be site blocking.

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