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The Effect of Chloride and Water Vapor on the Pt–Ir Interaction and IrO_2 Agglomeration in Bimetallic Pt–Ir Reforming Catalysts

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In addition to the air calcination temperature, the catalyst chloride level has been found to be one of the major factors affecting iridium agglomeration in Pt–Ir bimetallic catalysts. At a given air calcination temperature, there is a threshold chloride level below which agglomeration of iridium, which occurs in the form of large IrO_2 particles, increases with decreasing chloride level. The presence of water vapor during air calcination promotes IrO_2 agglomeration. The main function of water during calcination is to remove chloride from the surface of the catalyst. As the water vapor concentration in the calcination gas mixture is increased, more chloride is stripped from the catalyst, which leads to more IrO_2 agglomeration. © 1991 Academic Press, Inc.

INTRODUCTION

The effect of chlorine on activity and selectivity of reforming catalysts has been examined by numerous researchers (*1–5*). These studies report that the acidity of the catalyst increases with increasing Cl levels (*6, 7*). The acid cracking and the isomerization activities are thus influenced by the Cl level of the catalyst. Interaction between Cl and metal could potentially affect the coking on the catalyst surface. Indeed, Augustine *et al.* (*4*) have demonstrated that Cl affects the coking on both metal and support. While no effect was observed on the total amount of carbon retained on the catalyst, chloride, however, did increase the amount of coke on the support relative to that on the metal. Chloride-induced acidity is presumed to affect the mobility of the carbonaceous residues, causing them to remain on the support rather than move to the metal, and thus improving the activity maintenance.

Recently, Malet *et al.* (*2*) reported the effect of chlorine on the formation of Pt–Re alloys in Pt–Re/Al_2O_3 catalysts. Their studies suggest the presence of oxychlorinated Pt and/or Re species that interact strongly with a progressively dehydrated Al_2O_3 support. This process leads to higher metallic dispersions and lower Pt–Re alloying in chlorinated catalysts after hydrogen reduction.

We have reported earlier the effect of Pt–Ir interaction on Ir agglomeration, phase separation, and performance of the Pt–Ir/Al_2O_3 catalysts when they were subjected to different pretreatment conditions (*8*). We found that Pt–Ir interaction might be induced during the catalyst preparation. Direct air calcination of the impregnated catalysts maintains Pt and Ir in high oxidation states and, thus, direct calcination facilitates the formation of Pt–Ir mixed oxychloride and oxide complexes which stabilize iridium in a highly dispersed state since the formation of the IrO_2 phase is inhibited. However, reduction of the impregnated catalyst followed by air calcination causes a higher degree of IrO_2 agglomeration than direct calcination at the same temperature. Platinum and iridium in the hydrogen-reduced catalyst are in their metallic states forming highly dispersed bimetallic Pt–Ir

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clusters. The large difference in the reactivities of Pt and Ir toward oxidation results in the formation of the IrO_2 phase and its subsequent agglomeration. One obvious question to ask is the effect of catalyst regeneration on the stability of the highly dispersed iridium in the directly calcined catalyst after on-oil operation. It is expected that a regeneration by oxidation of this spent catalyst should result in a certain degree of IrO_2 agglomeration similar to that of the directly reduced and then calcined catalyst (fresh catalyst). This is because the platinum and iridium in the coked catalyst no longer exist as mixed oxychloride and oxide complexes, since they have been exposed to hydrogen during on-oil operation. Regeneration of the coked catalyst by oxidation at sufficiently high temperature promotes the formation of IrO_2 from Pt–Ir bimetallic clusters as illustrated in the above discussion of the reduced and calcined catalyst.

The purpose of this study was to further explore the effect of Cl on Pt–Ir interaction and IrO_2 agglomeration. The Pt–Ir/Al_2O_3 catalysts with different Cl levels were subjected to a 733 K O_2 calcination treatment to assess the effect of the Cl level on IrO_2 agglomeration. Additionally, the effects of water on the catalyst chloride level and on IrO_2 agglomeration have been investigated. The degree of IrO_2 agglomeration was assessed by Temperature-Programmed Reduction (TPR) and X-Ray Diffraction (XRD).

EXPERIMENTAL

Catalysts

The Pt–Ir/Al_2O_3 catalysts used in this study were prepared on gamma-Al_2O_3 supplied by Ketjen. Prior to use, the gamma-Al_2O_3 extrudates ($\frac{1}{16}$ in.) were calcined at 773 K for 6 h and ground to a particle size range of 40 to 80 mesh. The surface area of the support was near 190 m^2/g. Chloroplatinic and chloroiridic acids were used to prepare the electrolyte solutions, and their concentrations were adjusted to prepare 2.0 and 1.53 wt% loadings of Pt and Ir, respectively. The chloroplatinic acid solution was prepared by dissolving chloroplatinic acid crystals (supplied by Engelhard) in doubly distilled water. The chloroiridic acid solution containing 10.024 wt% Ir and 14.02 wt% Cl was supplied by Johnson and Matthey. Twenty grams of the meshed gamma-Al_2O_3 particles were immersed in 50 cm^3 of the impregnation solution, and the resulting slurry was shaken continuously for 24 h. The slurry was evaporated to dryness at room temperature over a 24-h period, and then dried in air at 393 K for an additional 16 h. The Cl level of the dry materials was 6%.

Three grams of dry precursor materials were calcined in a quartz tube furnace under a 20% O_2/He gas mixture with different water vapor concentrations at a total gas flow rate of 500 cc/min. Four H_2O vapor concentrations, 0, 0.2, 1, and 6%, were used in this study. The materials were brought to 393 K at a heating rate of 5 K/min and maintained at this temperature for 1.5 h. The temperature was then increased to 693 K at a heating rate of 5 K/min and held at this temperature for 4 h.

Three additional Pt–Ir catalysts with 2.41% Pt and 1.45% Ir were prepared with different amounts of HCl added to the H_2PtCl_6 and H_2IrCl_6 coimpregnation solutions to yield initial Cl levels of 11.10, 7.55, and 6.63%, respectively. These materials were air calcined in a muffle furnace employing procedures similar to those described above. A final calcination for 2 h at 773 K was carried out.

Temperature-Programmed Reduction

The apparatus used in this study consists of three major sections: gas purification/control system, reactor, and reactor assembly. Reactor temperature, controlled by an Omega temperature programmer, was measured at the center of the bed. Hydrogen consumption during TPR experiments was monitored by an IBM PC-XT interfaced to a Fisher Model 1200 gas partitioner with a built-in thermal conductivity cell. A more detailed description of the TPR apparatus can be found elsewhere (*8*).

One-hundred-milligram samples were dehydrated under Ar (100 cm^3/min) at 773 K (5 K/min) for 1 h. The samples were then allowed to cool to room temperature. The Ar stream was adjusted to 40 cm^3/min and directed to the TCD. After the TCD was stabilized, several pulses of 8.5% H_2/Ar were injected into the reactor via an internal 0.55 cm^3 sampling loop to assess the amount of H_2 consumption due to reduction of the samples at room temperature. The injection was repeated until H_2 breakthrough occurred.

The Ar stream was then switched to 8.5% H_2/Ar at a flow rate of 57 cm^3/min. After the TCD was stabilized, several pulses of Ar (0.55 cm^3) were injected into the reactor to calibrate the Ar pulse area and the time lag in the response time of the TCD to the Ar pulses. Ar pulse simulates the total H_2 consumption during TPO. After the TCD was calibrated, the temperature of the reactor was raised to 823 K at a heating rate of 20 K/min and held at 823 K for 30 min. The H_2 consumption data and temperature of the catalyst bed were recorded as a function of time.

X-Ray Diffraction Analysis

A Phillips Electronics X-ray diffractometer (XRG-3000) with nickel-filtered Cu$K\alpha$ radiation was used for X-ray diffraction studies of the samples. The relative amount of IrO_2 between samples was calculated from the area ratios of the IrO_2(110) line. XRD directly measures the agglomerated phase of IrO_2, and thus is more suitable than H_2 chemisorption.

RESULTS AND DISCUSSION

Effect of H_2O Level on IrO_2 Agglomeration and Cl Level

Figure 1 shows the XRD spectra of 2.0% Pt/1.53% Ir/Al_2O_3 catalysts subjected to different water vapor concentrations during 693 K calcination. The intensities of the IrO_2 (110), (101), and (211) peaks increase with increasing water vapor concentration during the calcination. Figure 2 shows that the degree of IrO_2 agglomeration, calculated from the (110) peak, increases with increasing water vapor concentration. One hundred percent IrO_2 agglomeration was assumed when the same catalyst was subjected to 24 h of calcination at 813 K in a muffle furnace. Figure 2 also shows that the final Cl level on the catalyst after calcination decreases with increasing water vapor concentration. The Cl level was determined by X-ray fluorescence spectroscopy. Higher water vapor concentrations in the calcination gas mixture result in more Cl stripping from the catalyst surface.

Figure 3 shows that the degree of IrO_2 agglomeration decreases linearly with increasing final Cl level on the catalyst. This finding supports our previous proposal that Cl interacts with Pt and Ir to form mixed oxychlorides and oxides in an oxidizing environment. Therefore, the main function of water during the calcination is to remove chloride from the surface of the catalyst. The higher the Cl level on the catalyst, the less the degree of IrO_2 agglomeration. It appears that chloride level on the catalyst and calcination temperature are the major factors affecting IrO_2 agglomeration. This argument is further supported by the results shown below when the catalysts with various Cl loadings are subjected to a higher temperature, 733 K, air calcination.

The Effect of Cl Level on Agglomeration

Another way to obtain different final chloride levels is to dose a catalyst with various amounts of HCl. Figure 4 shows the TPR spectra of such air-calcined catalysts. Their initial Cl levels were 11.10, 7.55, and 6.63%, and decreased to 3.25, 2.87, and 2.90%, respectively, after air calcination at 733 K. The TPR spectra of the calcined catalysts generally exhibit the same three-peak pattern, but the degrees of

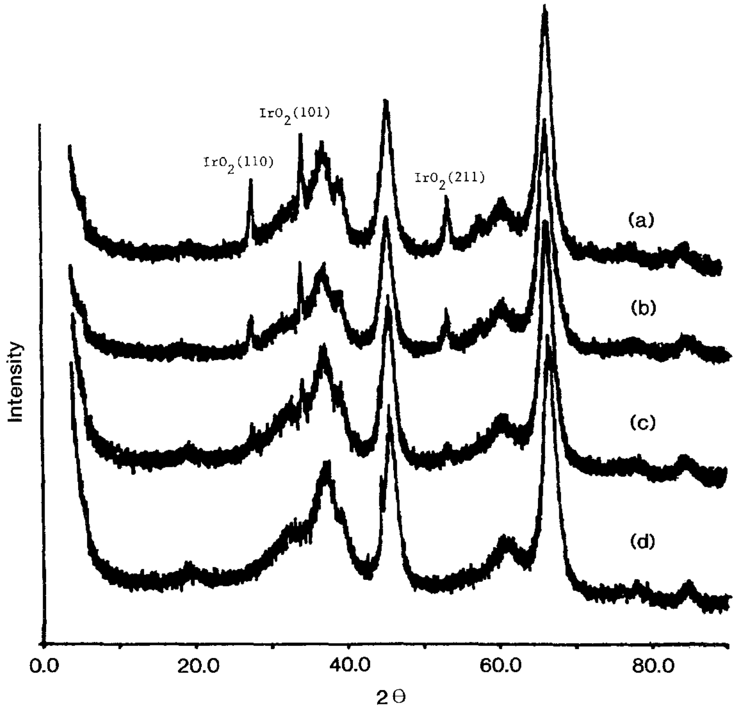


FIG. 1. X-ray diffraction spectra of 2.0% Pt/1.53% Ir/Al_2O_3 catalysts subjected to the water vapor concentration of (a) 6%, (b) 1%, (c) 0.2%, and (d) 0% respectively, during 693 K calcination.

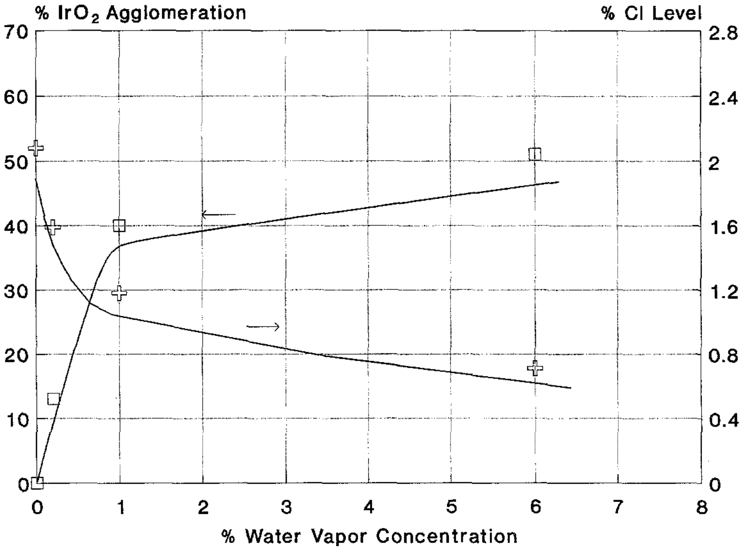


FIG. 2. Effect of water vapor concentration during calcination on IrO_2 agglomeration and final Cl level.

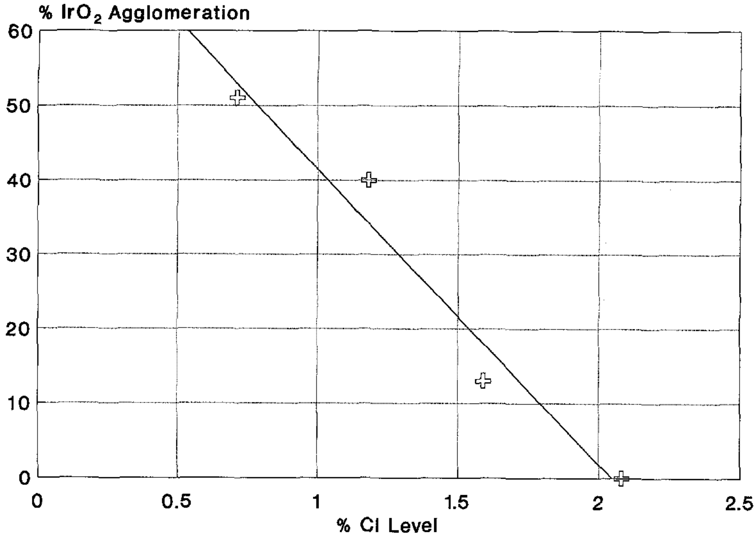
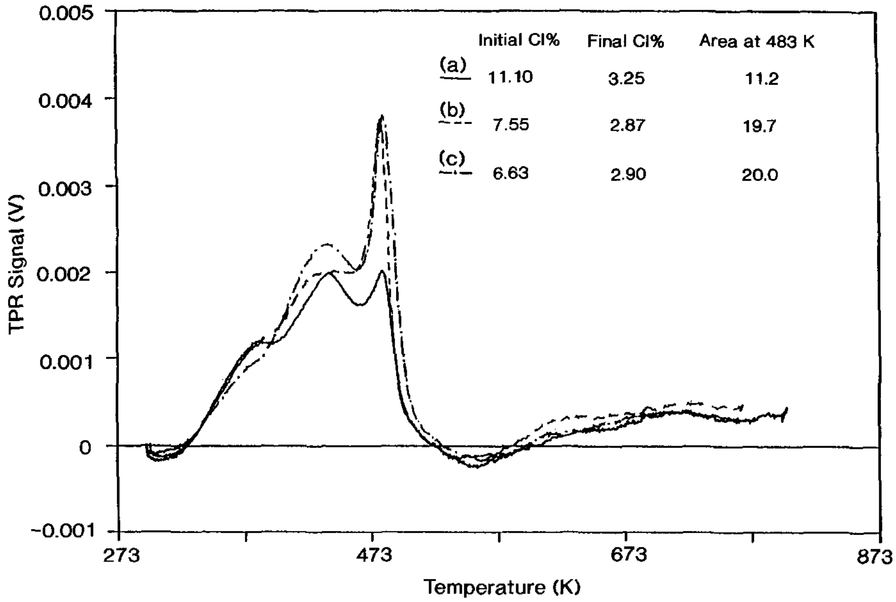


FIG. 3. Plot of IrO_2 agglomeration vs final Cl level.

IrO_2 agglomeration are different among the catalysts. In the previous report (*8*), we identified the TPR peaks observed at about 373, 433, and 483 K were due to the highly dispersed Pt^{2+}, the highly dispersed Pt^{4+} and/or bimetallic Pt–Ir oxygen-rich complexes, and agglomerated IrO_2, respectively. The existence of the agglomerated IrO_2 particles can be easily identified by their sharp reduction peak at about 483 K in the TPR spectrum. A Gaussian distribution function was used to separate the overlap-



	Initial Cl%	Final Cl%	Area at 483 K
(a) ——	11.10	3.25	11.2
(b) – – –	7.55	2.87	19.7
(c) —·—	6.63	2.90	20.0

FIG. 4. TPR spectra of the catalysts with initial Cl levels of (a) 11.10%, (b) 7.55%, and (c) 6.63% Cl, respectively.

ping peaks. It was found that the fraction of total area for the peak at 483 K was 11, 20, and 20% for the catalysts with final Cl levels of 3.25, 2.87, and 2.90%, respectively. Thus a 40 K increase in the calcination temperature promoted IrO_2 agglomeration even though the catalysts retained 2.9 to 3.25% Cl, which is higher than the 2.1% Cl retained on the lower temperature calcined sample. Significantly, this lower temperature calcined sample showed no IrO_2 agglomeration.

X-ray diffraction measurements on the Pt–Ir/Al_2O_3 catalysts with initial Cl levels of 11.1 and 6.63% showed the same trend as that observed in TPR experiments, i.e., a higher initial Cl level on the catalyst results in a lower degree of IrO_2 agglomeration after air calcination at 733 K. In our previous paper (*8*), we also demonstrated that a higher calcination temperature yielded a higher degree of IrO_2 agglomeration. Thus, a higher calcination temperature would require a higher Cl level to suppress IrO_2 agglomeration.

We reported in the previous paper (*8*) that the degree of IrO_2 agglomeration of the 693 K calcined Ir/Al_2O_3 catalyst was much larger than that of Pt–Ir/Al_2O_3 catalysts. It indicated that the Pt–Ir interaction reduced the degree of IrO_2 agglomeration. Chloride promotes the interaction between Pt and Ir to form mixed oxychlorides and oxides in an oxidizing environment. The effect of Cl on IrO_2 agglomeration is, therefore, more significant for the Pt–Ir/Al_2O_3 catalyst than the Ir/Al_2O_3 catalyst, which has no Pt–Ir interaction.

The results shown above suggested that at a given air calcination temperature and a given iridium loading there is a threshold Cl level below which IrO_2 agglomeration occurs and agglomeration increases with decreasing Cl level. This finding is similar to the data reported by Fung *et al.* (*9, 10*) on the influence of catalyst Cl level on IrO_2 agglomeration during redispersion of iridium-containing catalysts. At 693 K air calcination temperature, Cl to metal weight ratio, Cl/*M*, of 0.6 (2.1% Cl/3.53% Pt–Ir) or greater is required to avoid IrO_2 agglomeration. An increase of Cl/*M* from 0.6 to 0.84 (3.25% Cl/4.86% Pt–Ir) is not sufficient to counteract an increase in the calcination temperature by 40 K to 733 K which results in 11% IrO_2 agglomeration. McVicker and Ziemiak (*11*) employed X-ray diffraction and H_2 and CO chemisorption in their studies of the agglomeration behavior of a commercial Pt–Ir catalyst (0.3% Pt–0.3% Ir and 0.67% Cl) showed that 4-h air calcination at 773 K resulted in 58% IrO_2 agglomeration. The Cl/*M* ratio in this case is 1.1. Therefore, a substantial increase in the Cl/*M* ratio is required to suppress IrO_2 agglomeration when the calcination temperature is greater than 733 K.

The presence of a large number of excess Cl ions on the support may result in a close interaction between the Pt and Ir oxychlorides. On the other hand, this study also indicates the precautions that one has to take when preparing Pt–Ir catalysts. A subtle difference in water concentration during air calcination would result in a large change in catalytic properties.

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