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Redispersion of iridium using in situ chlorine generation and avoiding iron contamination

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Abstract

Previously we showed that because of the high susceptibility of iridium to oxidative agglomeration, direct application of the Pt/γ-Al_2O_3 regeneration procedure to Pt-Ir/γ-Al_2O_3 reforming catalysts is ineffective [1]. Special considerations are needed to ensure that the agglomerated Ir particles are in their metallic state in order to facilitate iridium redispersion. Further advances in our understanding of the redispersion chemistry resulted in an iridium redispersion technology replacing elemental chlorine with chlorine containing compounds. However, iron contamination of the catalyst extrudates was observed when iron scale were present in the catalyst bed. The iron scale formed in the furnace tubes because of exposure to sulfur and the oxidation and reduction environment encountered during catalyst regeneration. The critical sequence of steps leading to iron transfer in the regeneration of iridium containing catalysts has been identified. These involve the reduction of Fe_2O_3 to Fe_3O_4 and metallic iron and their reactions with HCl during the HCl saturation step forming mobile divalent iron chloride species, which transfer to the catalyst extrudates through physical contacts. Successful modifications to the regeneration procedure result in high iridium redispersion and essentially no iron transfer. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Iridium redispersion; Agglomeration; Pt-Ir/γ-Al_2O_3; Iron contamination; Catalyst regeneration; Iron transfer

1. Introduction

As noted in our paper [1], the reaction chemistry of the alumina support with the reactive gases, chlorine and hydrogen chloride greatly influences iridium redispersion. Understanding of the redispersion chemistry allows us to adapt the conventional Pt/γ-Al_2O_3 chlorine redispersion procedure to Pt-Ir/γ-Al_2O_3. This understanding further advances the redispersion technology of iridium containing catalysts by eliminating the external supply of elemental chlorine through in situ chlorine generation (from oxygen and chlorine containing compounds) which previously was considered utterly impossible [2,3]. However, in a commercial reformer, iron scale can enter the catalyst bed. When iron scale are in contact with the catalyst extrudates, iron contamination of the catalyst extrudates occurs during catalyst redispersion and adversely affects the activity of the regenerated catalyst because it binds to the acid sites and alloys with the noble metals. The aim of the present work is to describe how we, through the understanding of the redispersion chemistry involving iridium and iron, develop effective redispersion procedures which minimize iron contamination and eliminate the use of elemental chlorine.

2. Experimental

2.1. Reactor and catalyst loading

An atmospheric reactor was used in this regeneration and redispersion study. The reactor was a 91.4 cm quartz tube of 2.9 cm I.D. The outlet of the reactor con-

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sisted of three quartz tubes of 0.38 cm I.D. extended into the catalyst bed. The three tubes were different in lengths. The longest one extended to about 6.4 cm upstream of the first catalyst section to monitor the inlet gas composition. The shortest tube was located at the bottom of the third catalyst section. The medium length tube was situated at the bottom of the first catalyst section. The gas flow rate in each of the outlet tubes was less than 5% total gas flow to avoid a significant change in the space velocity. The outlets of these tubes were connected to a GC valve through a stream selection valve so that the gas phase composition along the catalyst bed could be monitored by a thermal conductivity detector (TCD) during redispersion. A 6.1 m long and 3 mm I.D. column packed with 10% QF-1 on 40/60 mesh Chromosorb T showed adequate separation among O_2, HCl, Cl_2 and H_2O. Preconditioning of the column with HCl and Cl_2 was necessary to give stable operation. The column was conditioned at 90°C with injection of 1 cm^3 gas sample containing 1 vol% Cl_2 and 1 vol% HCl. Satisfactory performance was obtained at a column temperature of 30°C and a helium flow of 50 cm^3/min. Quartz wool plugs of about 0.85 cm thick were used as spacers to separate the three catalyst sections. Each catalyst sections contained 20 g of 0.16 cm catalyst extrudates with a composition of 0.3 wt.% Pt-0.3 wt.% Ir/γ-Al_2O_3. The multistep regeneration and redispersion experiments were carried out at temperatures from 280–520°C as specified. Concentrations of Cl_2 and HCl lower than 2000 vppm are used in commercial operation to minimize corrosion and disposal problems. Commercial reactor pressure is general around 0.35–1.0 MPa. Therefore, the concentrations of Cl_2 and HCl in our atmospheric lab reactor is 1 vol% or below to maintain the same partial pressure. The gas flow rate was between 100 to 500 cm^3/min.

To simulate the iron particles present in a commercial reactor, two different kinds of iron particles were used in this study. They were iron metal filings, greater than 250 μ and Fe_2O_3 fine powder, less than 100 μ. The iron filing particles were covered with a thin oxide layer since they had been exposed to air at ambient condition. Fe_2O_3 fine powder was the most suitable iron compound for this study since it formed a fairly uniform coating on the catalyst extrudates when a weighted amount of Fe_2O_3 was mixed and shaken with the extrudates. In contrast, iron filings did not adhere to the extrudates. Because of their higher bulk density, iron filings had the tendency to gravitate together even when they were sprinkled onto a packed catalyst bed. Therefore, their contact with the extrudates was much less than that of Fe_2O_3 when they were compared at the same weight percent loading. Iron loading on the extrudates was 1 wt.% Fe for iron filings and 2 wt.% Fe (as metallic iron) for Fe_2O_3 powder. This level of iron loading is expected in a commercial reactor with periodic dumping and screening of the catalyst extrudates to remove iron scale. In the case of coated catalyst extrudates, the actual iron loading might be somewhat less than the intended 2 wt.% Fe since some Fe_2O_3 powder remained in the mixing vessel. A different loading method was employed for iron filings. They were loaded into a packed catalyst bed in a multilayer manner. However, there was still a high tendency for the iron filings to penetrate the catalyst bed but they were retained by the quartz wool plug which was employed to separate the catalyst sections. In some experiments, in addition to the three catalyst sections loaded with iron, a packed bed of iron filings was placed just upstream (separated by a 0.85 cm quartz wool plug) of the first catalyst section to simulate the extent of iron contamination due to corrosion of the gas distributor and the reactor wall. The first catalyst section, in this case, initially contained no iron oxide particles. Iron contamination in this catalyst section, if it occurred, was due to vapor transport of the corrosion product from the packed iron bed. In contrast, iron contamination in the catalyst sections containing iron filings and iron oxide powder might occur under certain reaction conditions where there was no vapor phase corrosion products (i.e., negligible corrosion of the distributor or reactor wall). The transfer of iron in this case was through physical contact between the catalyst extrudates and the iron particles.

2.2. Determination of Ir agglomeration

A convenient way to determine the degree of metal agglomeration is by X-ray powder diffraction. A Philips Electronics X-ray diffractometer (XRG-3000) with nickel filtered CuK radiation was used. Percent IrO_2 and Ir agglomerations on a redispersed Pt-Ir catalyst were calculated from the area ratios of IrO_2 and Ir X-ray peaks between the redispersed catalyst and two standard catalysts with all their iridium agglomerated as IrO_2 and Ir respectively. Air calcination of the fresh catalyst at 540°C for 16 h generated the 100% agglomerated IrO_2 standard where the IrO_2 crystallites are about 400 Å. Hydrogen treatment of the IrO_2 standard at a temperature >450°C converted IrO_2 to the agglomerated Ir standard. The presence of Fe_2O_3 interferes with Ir metal agglomeration determination since one of the Fe_2O_3 X-ray peaks overlaps significantly with the Ir 111 peak. Close to complete removal of Fe_2O_3 is required to obtain accurate Ir metal agglomeration determination.

2.3. *Determination of amount of iron transferred to the catalyst extrudates*

In this study, we want to determine the amount of iron, which has been chemically bound to the catalyst extrudates after the redispersion treatment. Iron particles, which physically adhered to the catalyst extrudates, interfered with the above evaluation. A convenient way to remove the physically adhered iron particles is by sonic vibration. The discharged catalyst was transferred into a beaker containing acetone. The beaker was subjected to sonic vibration for 20 min. The vibration dislodged the iron particles from the extrudates. Iron contamination in the sonically cleaned extrudates represented iron chemically transferred to the alumina extrudates due to reactions between iron and the chlorine containing gases. The iron content and the chloride level in the catalyst were determined by X-ray fluorescence. The determined iron concentration was expressed as the amount of Fe (did not include the anions) contained in the catalyst extrudates. The crystalline phases of the iron particles after a treatment step were determined by X-ray diffraction.

3. Results and discussion

3.1. *Direct application of Pt redispersion technology to Ir encountered problems*

The regeneration and redispersion of agglomerated Pt/Al_2O_3 catalysts are well established. The coke on the catalyst can be burned off at a temperature below 500°C. Then the catalyst can be redispersed at 425–530°C using chlorine in the presence or absence of oxygen [4] or in situ generated chlorine, i.e., a chlorine containing compound and oxygen [5,6]. However, previous attempts in direct application of the Pt redispersion methods, i.e. after coke burn, the catalyst is treated with chlorine [7–9] or in situ generated chlorine [3], to Pt-Ir catalysts were unsuccessful in redispersing agglomerated iridium particles. Bishara et al. [3] reported that the dispersion of a $Pt\text{-}Ir/Al_2O_3$ catalyst after coke was burned off depended on the amount of CCl_4 injected in the $CCl_4 + O_2$ treatment step. The maximum metal dispersion determined by chemisorption was 55%. This indicates that only Pt was redispersed to a highly dispersed state and Ir was still agglomerated. Therefore, the traditional in situ chlorine generation cannot redisperse Ir agglomerates. Our early paper [1] has identified that the high sensitivity of iridium to oxidative agglomeration by oxygen is the main reason why the conventional Pt redispersion procedure is ineffective in redispersing iridium agglomerates.

3.2. *Non-steady state period reaction chemistry greatly affects iridium redispersion*

Unlike the familiar catalytic reactions, wherein reactants are all gas phase species, redispersion of agglomerated metal catalysts involves the direct reaction between the catalyst and the reactive gaseous components such as Cl_2, HCl and O_2. Additionally, the reactive gaseous components in the redispersion media generally are low in concentrations to minimize corrosion. The catalyst support has a high-reactive capacity toward some of the reactive gaseous components and delays their movement down the catalyst bed. Thus, the non-steady state condition (before Cl_2 or HCl exits the catalyst bed) in catalyst redispersion is significantly longer than the conventional catalytic reaction. Its effect on metal redispersion can be critical because the metal particles down stream of the bed entrance can be exposed to reaction products and at the same time deprived of the reactive redispersion gas, chlorine.

3.2.1. *Detrimental effect of oxygen*

Fig. 1A shows the gas phase composition at the reactor exit as a function of chlorine treatment time

Table 1

Benefits of HCl pretreatment before redispersion of 0.3% Pt-0.3% Ir/γ-Al_2O_3 catalysts where 80-100% of its iridium is agglomerated as large IrO_2 particles. Reaction conditions: 520°C, atmospheric pressure

Run #[a]	Treatment steps before redispersion	Wt.% Cl on cat before redispersion	Redispersion step	Redispersion time min.	% Residual Ir (IrO_2) agglomeration In/Mid/Out
1	H_2 Reduction	0.6	1% Cl_2 + 1.4% H_2O	55	74/73/67 (0/0/9)
2	1. H_2 Reduction 2. 1% HCl + 1% H_2O	1.9	1% Cl_2 + 1.4% H_2O	20	37/36/36 (0/0/0)
3	1. H_2 Reduction 2. 1% HCl + 1% H_2O	1.9	0.3% Cl_2 + 6% O_2	60	0 (0)
4	1. H_2 Reduction 2. 1% HCl + 1% H_2O	1.9	0.3% Cl_2	60	71 (0)
5	1. H_2 Reduction 2. 1% HCl + 1% H_2O	1.9	0.8%HCl + 12% O_2	69	0/0/0 (0/0/0)

[a] Run 1, 2 and 5 with three catalyst sections, Run 3 and 4 with one catalyst section. 20 g catalyst extrudates in each section. Initial iridium agglomeration in Run 1 and 2 is 80% and in Run 3, 4 and 5 is 100%. Catalyst chloride content after redispersion is 2.0–2.1 wt.%.

of Run 1 in Table 1. The catalyst with 80% iridium agglomerated as IrO_2 (i.e., the rest of iridium remained highly dispersed) and 0.60 wt.% chloride was first reduced at 520°C. Then the treatment gas was switched to a chlorine containing gas at a flow rate of 100 cm^3/min with a composition of 1 vol% Cl_2, 1.4 vol% H_2O and 97.6 vol% helium. For about 43 min after the introduction of chlorine there was no chlorine at the exit of the catalyst bed. On the other hand, oxygen at 0.42% and water in excess of 1.4% (water not shown in the figure) were detected much earlier. The observed gas phase composition-time profile in Fig. 1A can be rationalized in view of Fig. 1B. Fig. 1B shows what happened to the catalyst during the chlorine treatment. At the entrance of the catalyst bed chlorine was depleted rapidly to a near zero value because it reacted quantitatively with Al_2O_3 at a high rate and liberated oxygen according to reaction A. The generated oxygen quickly moved down the catalyst bed and was detected at the reactor outlet. However, the chlorine front moved very slowly down the catalyst bed because the incoming chlorine was rapidly captured by the alumina at the bed inlet. The downstream movement of the chlorine front and reaction A commenced only after the upstream portion of the alumina had increased its chloride level from 0.6 to 1.9 wt.% via reaction A. From the stoichiometry of reaction A, one may expect a maximum of 0.5% O_2. The observed oxygen concentration, 0.42%, is close to the expected value. In a duplicate experiment, oxygen breakthrough time was determined by continuous monitoring oxygen at the reactor outlet from the start of the chlorine treatment step. It was found that oxygen breakthrough was delayed by about 6.5 min beyond the time needed for the oxygen to travel the catalyst bed. This was most

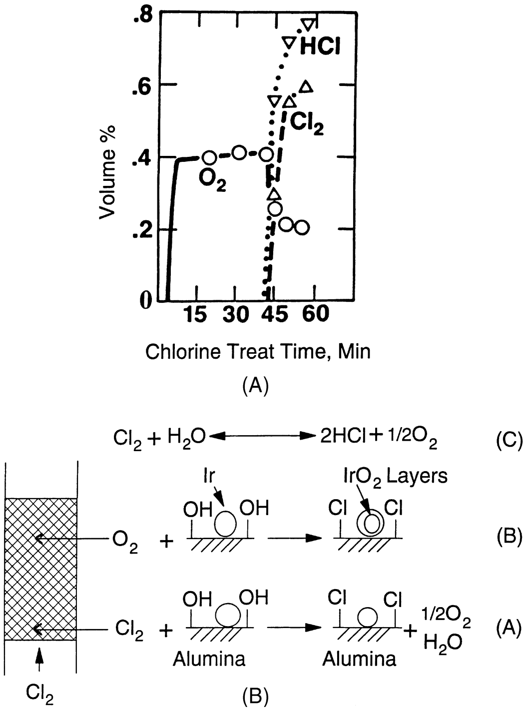

Fig. 1. Wet chlorine redispersion of agglomerated Ir in 0.3% Pt-0.3%Ir/γ-Al_2O_3 at 520°C after hydrogen reduction. 1A: Gas phase composition at reactor outlet, 1B: Reactions taking place at the catalyst surfaces.

probably due to the reaction between oxygen and the reduced metal particles as indicated by reaction B (Fig. 1B). The absence of chlorine further along the bed, especially at the exit section of the catalyst bed, permitted oxygen to form the oxide layer on the iridium agglomerates, and to form IrO_2 agglomerates from the remaining highly dispersed iridium, thus, preventing their redispersion when chlorine did eventually come in contact with them. It has been previously reported [1,10] that large Ir metal particles when exposed to oxygen at high temperatures do not bulk oxidize, i.e., X-ray diffraction pattern shows only Ir metal peaks. This explains why there was no significant decrease in the percent of Ir metal agglomeration and the appearance of IrO_2 agglomerates in the catalyst at the outlet section of Run 1 after the conventional Pt/Al_2O_3 redispersion procedure was applied to the $Pt\text{-}Ir/Al_2O_3$ catalyst.

After chlorine was detected at the reactor exit, the exit gas phase composition shown in Fig. 1A was governed by reaction C in Fig. 1B. Reaction C is relatively slow and requires the whole catalyst bed to attain equilibrium conversion of the reactants: chlorine and water. Good agreement was obtained between the gas phase composition (Fig. 1A) and the stoichiometry of reaction C. For example, 8 min past chlorine breakthrough the gas phase composition at the exit revealed that about 0.4% Cl_2 was reacted and 0.21% O_2 and 0.78% HCl were produced. Although there is a volume increase in reaction C (from 2 mol of gas to 2.5 mol) the very dilute nature of the reactants minimize the volume change and therefore, the observed concentrations can be used directly to calculate the reaction stoichiometry.

3.2.2. *Beneficial effect of oxygen*

A highly effective way to achieve chloride saturation without exposing Ir particles to oxygen during the non-steady state period is illustrated by Run 2. After the hydrogen reduction step, the catalyst was treated with 1 vol% HCl and 1 vol% H_2O in helium. The reaction between HCl and the alumina support is depicted by reaction D in Fig. 2B which indicates H_2O is the sole gas phase product. Since high chloride demand by the support had been satisfied after the HCl treatment, chlorine breakthrough became much faster. It took less than 10 min to observe Cl_2 at the reactor outlet (Fig. 2A). A much higher redispersion was obtained (Table 1) though there was 0.21 vol% oxygen detected at the reactor outlet due to reaction C. The presence of oxygen during chlorine redispersion of a chloride saturated catalyst and of a chloride deficient catalyst apparently leads to vastly different results. It appears that a certain minimum ratio of chlorine to oxygen is required to prevent the formation of IrO_2 agglomerates and oxide layers on Ir agglomerates. Instead, it may form oxychlorides on the surface of Ir agglomerates (reaction E in Fig. 2B). The oxychlorides may have high mobility to facilitate redispersion of iridium. Most probably, chlorine is generated from catalyst chloride when the catalyst is exposed to oxygen and its concentration is proportional to the chloride content on the catalyst. Exposure of the decoked catalyst which has low level of chloride, 0.6–0.8 wt.% Cl, to oxygen at high temperature permits oxygen to form the oxide layer on the iridium agglomerates and to agglomerate the remaining highly dispersed iridium

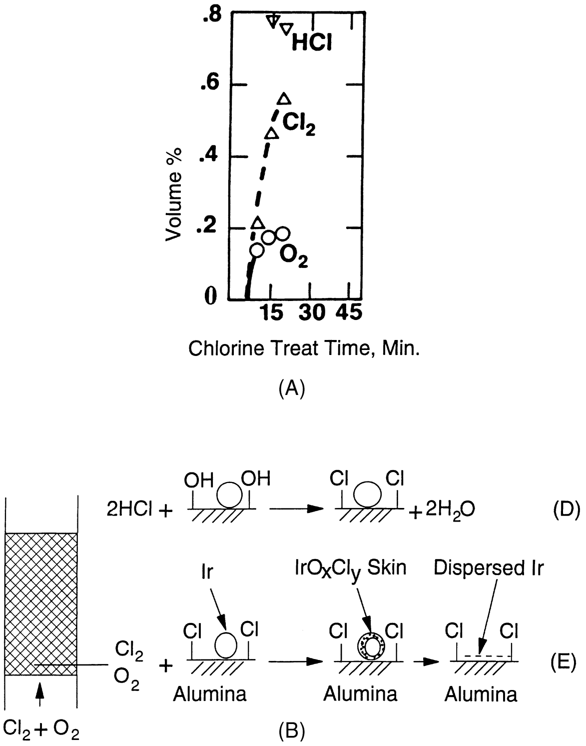

Fig. 2. Wet chlorine redispersion of agglomerated Ir on 0.3%Pt-0.3%Ir/γ-Al_2O_3 at 520°C after hydrogen reduction and HCl saturation. 2A: Gas phase composition at reactor outlet, 2B: Reactions taking place at the catalyst surfaces.

to IrO_2 agglomerates because the chlorine to oxygen ratio is low.

When catalyst chloride is high, as after a HCl saturation step, the presence of oxygen in the chlorine treatment step greatly facilitates Ir redispersion so that chlorine concentration can be reduced and still provides high degree of Ir redispersion. Run 3 in Table 1 shows that in a dry chlorine redispersion of a HCl saturated catalyst, the addition of 6% oxygen to the 0.3% chlorine stream gives 100% iridium redispersion in one hour compared to 29% iridium redispersion when oxygen is not used (Run 4). Since high concentration of oxygen can be used after the catalyst is saturated with chloride one can generate chlorine in situ and eliminate the use of elemental chlorine. Table 1 shows the effectiveness of $HCl + O_2$ redispersion (Run 5). Complete redispersion of 100% Ir agglomerates is attained after 69 min with 0.8% HCl and 12% O_2.

3.3. *Dry chlorine in the absence of oxygen corrosively attacks iron metal and iron is vapor transported to catalyst extrudates*

Though we have demonstrated that the above in situ chlorine generation procedure is very effective in redispersing agglomerated iridium, applying it to a commercial reactor requires that the procedure does not produce intolerable corrosion of the gas distributor and the reactor vessel (less than 0.5 μ loss in metal thickness per redispersion operation) and iron contamination to the catalyst. Iron contamination lowers the activity of the catalyst. It is well known that dry chlorine (without oxygen) is very corrosive toward carbon steel at high temperatures due to the formation of highly volatile $FeCl_3$. This is demonstrated by the experiment (Run 6) shown in Table 2. The catalyst was loaded in the reactor according to the following configuration. Upstream of the first catalyst sections there was a packed iron filing bed (FeFilings) of 0.5 g. We have to emphasize that the first catalyst section (Cat), next to the iron filing bed, contained no iron. The second catalyst section mixed with 0.2 g iron filings (Cat-FeFilings) and the third section catalyst was coated with Fe_2O_3 to give 2 wt.% Fe ($CatFe_2O_3$). The above loading configuration shows how iron is being transfer to the catalyst extrudates: via gas phase transport or through physical contacts, and the dependency of iron transfer on iron oxidation state. Each of the bed-sections was separated with 0.85 cm quartz wool plugs. After the catalyst was reduced with hydrogen at 510°C, chlorine in helium at 0.86% was introduced into the reactor. It took 104 min before chlorine was detected at the reactor exit and the chlorine treatment was continued for an additional 44 min. Catalyst particles in the front 2/3 of the first catalyst section (originally containing no iron particles) were coated with 2.6 wt.% Fe which was deposited onto the catalyst by vapor transport from the upstream packed bed of iron filings. There was little material left in the iron filing bed. Very little iron is detected on the catalyst extrudates in the second section where catalyst extrudates were mixed in with iron filings (after sonic separation to remove non-chemically bound iron). The different corrosion response of iron filings exhibited in the packed iron bed and in the second catalyst section was most probably due to reoxidation of the iron filings in the second catalyst section by oxygen generated when chlorine reacted with alumina in the first catalyst section. The standard free energies of reaction (1) and (2) have been calculated at 510°C based on the standard free energies values of chemical compounds reported by Reed [11] and Wicks and Block [12]. The highly positive standard free energies of reaction (1) and (2) suggest that Cl_2 corrosion attack of iron oxides by vapor phase transport (forming $FeCl_3$) is not possible since according to reaction (1) when Cl_2 concentration is 1 vol%, O_2 level has to be 6.5×10^{-20} vol% to have both Fe_2O_3 and $FeCl_3$ present.

$$Fe_2O_3 + 3Cl_2 = 2FeCl_3 + \tfrac{3}{2}O_2$$
$$\Delta G_{510^\circ C} = +35.5\,\text{kcal/mol} \tag{1}$$

$$Fe_3O_4 + \tfrac{9}{2}Cl_2 = 3FeCl_3 + 2O_2$$
$$\Delta G_{510^\circ C} = +37\,\text{kcal/mol} \tag{2}$$

In contrast, the packed iron bed was upstream of the catalyst sections and therefore iron particles remain as metallic iron and reacted with chlorine to produce corrosion product $FeCl_3$. There was appreciable iron transfer to the catalyst extrudates in the third section. It amounted to 0.79 wt.% Fe. It appeared that the quantity of in situ generated oxygen was not enough to oxidize all the reduced iron powder in the third catalyst section. This is supported by the lack of a distinct oxygen breakthrough at the reactor exit.

Table 2
Reactions of iron and iron oxides with Cl_2 and HCl

Run #[a]	Treatment steps before redispersion	Redispersion step	wt.% Fe on cat sections after sonic cleaning
6	H_2 Reduction	0.86% Cl_2	–/2.6[b]/0.01/0.79
7	1. H_2 Reduction 2. 1% HCl	0.3% HCl + 8% O_2	–/0.05/0.21/1.65
8	1. H_2 Reduction 2. 0.92% HCl	None	–/0/1.71/1.75

[a] Catalyst loading: Run 6 and 7, FeFilings/Cat/Cat-FeFilings/CatFe_2O_3; Run 8, FeFilings/Cat/CatFe_2O_3/CatFe_2O_3.

[b] Iron content of front 2/3 of cat bed.

3.4. *In situ chlorine generation eliminates iron contamination by vapor transport but iron is transferred by contact*

Run 7 in Table 2 shows that replacing the dry chlorine with dry HCl + O_2 inhibited the formation and the transport of vapor phase corrosion products. The catalyst loading configuration in the reactor is the same as the chlorine redispersion experiment in Section 3.3. After the hydrogen reduction the catalyst was treated with 1% HCl to saturation at 510°C before the HCl + O_2 (0.3% HCl and 8% O_2) redispersion step. Very little iron was vapor transported from the iron packed bed to the first section catalyst extrudates. The iron packed bed actually gained close to 40% in weight after the redispersion treatment. X-ray diffraction indicated Fe_2O_3 and Fe_3O_4 were the major phases. Metallic iron peaks and peaks belonging to $FeCl_2 \cdot 4H_2O$ (water is one of the reaction product) were detected. Iron contamination in the first catalyst section was observed only on the few extrudates located at the very front of this section. Within each extrudate the iron contamination was nonuniform. The overall iron content in this first catalyst section was 0.05 wt.%. However, there was appreciable iron transfer by contact in the third catalyst section where the catalyst extrudates were in intimate contact with fine Fe powder which was the product of the reduction of Fe_2O_3. Iron content in this section was 1.65 wt.%. The catalyst extrudates had a fairly uniform light brown coating on their outside surface. No metallic iron or iron compounds were detected by X-ray diffraction suggesting iron was highly dispersed on the Al_2O_3 support. The thickness of the iron layer on the extrudates was about 60 μ as is determined by electron microprobe analysis. Much reduced iron transfer was observed in the second section due to a substantial reduction in the number of contacts between iron fillings and the extrudates as discussed earlier. It may also have a contribution from a slower reaction rate because the much larger size of the iron filling particles. Iron contamination in this section was highly non-uniform. It occurred where the catalyst extrudates were in close contact with the iron filings. The overall iron content in this section was 0.21 wt.%. Lowering the oxygen concentration or the addition of 1% water in the HCl + O_2 treatment step (maintaining the same HCl saturation step) did not affect the level of iron transfer to the catalyst in the third section.

Though the HCl + O_2 procedure inhibits the corrosion through vapor transport of corrosion products from the gas distributor and reactor wall to the catalyst extrudates, the degree of iron transfer due to contacting is actually higher than in the dry chlorine treatment (compare the third catalyst section in Run 6 and 7). Iron exposure to in situ generated oxygen during dry chlorine redispersion was used in the previous paragraph to explain the lower degree of iron transfer in the second and third sections. However, during the HCl + O_2 redispersion iron was exposed to a much higher oxygen concentration than in the dry chlorine treatment but the beneficial effect of oxygen was not observed. This contradiction is resolved when the critical step in iron transfer during the HCl + O_2 redispersion is identified, and it is discussed in the following section.

3.5. *Critical steps in iron transfer during HCl + O_2 redispersion*

In order to understand why the presence of oxygen in the catalyst redispersion step (HCl + O_2) does not prevent iron transfer, one has to identify at which step or combination of steps in the redispersion procedure iron transfer occurs. The first step in the redispersion is hydrogen reduction at 510°C. We do not expect any chemical transfer of iron to the extrudates during the reduction step. However, physical adhesion of iron onto the extrudates increases with reduction temperature. When the extrudates, which were coated with Fe_2O_3 powder, were hydrogen reduced at 247°C for 2 h, about 1 wt.% iron was retained in the extrudates even when the sample was washed with acetone several times. Much better removal of iron was achieved when the sample was submerged in acetone and subjected to sonic vibration. The iron content of the extrudates after sonic cleaning was 0.04 wt.%. At a higher reduction temperature of 350°C and 500°C, the iron content of the sonic cleaned extrudates increased to 0.10 wt.% and 0.24 wt.% respectively. However, the X-ray spectra of these samples revealed no peaks, which belong to metallic iron, or any iron compound indicating that this level of iron loading is below the detection limit.

After hydrogen reduction the catalyst was treated with 1% HCl in helium to increase catalyst chloride before the redispersion step, i.e., $HCl + O_2$. Iron transfer may occur during this HCl saturation step. This was investigated in Run 8 in Table 2. Catalyst loading configuration in this run was the same as the previous runs except catalyst in the second section was coated with Fe_2O_3 to 2 wt.% Fe instead of mixing with iron filings. The reduced catalyst was treated with 0.92% HCl to HCl breakthrough plus 30 min. X-ray diffraction indicated that the packed iron filing bed was a mixture of metallic iron and $FeCl_2{\cdot}2H_2O$ in comparable quantities. There was no iron contamination in the first catalyst section because there was no corrosive loss of iron in the up-stream iron filing bed. The iron content on the second and the third catalyst sections were 1.71 and 1.75 wt.% respectively. The outside of the extrudates was uniformly light brown in color. The iron compound appeared to be highly dispersed on the Al_2O_3 support since no X-ray diffraction peak of iron or iron compound is detected. Therefore, the critical sequence of steps in iron transfer is the reduction of iron oxide to metallic iron and its reaction with HCl to form mobile divalent iron chloride species. Exposure of these iron-contaminated extrudates to oxygen and HCl in the subsequent redispersion step such as Run 7 resulted in no additional iron transfer. Furthermore, it appeared there was no appreciable change in the chemical state and physical state of this highly dispersed iron after oxygen exposure since the catalyst extrudates had the same color and the iron compounds remained amorphous to X-ray diffraction. This indicates a strong interaction between the transferred iron species and the alumina support.

3.6. Reaction chemistry between HCl and metallic iron and iron oxides

From the available thermodynamic data, we want to investigate under what conditions the formation of ferrous chloride may be suppressed so that we can inhibit iron transfer to the catalyst extrudates. The following reactions are considered since the iron scale in the reactor is in the form of iron metal or iron oxides depending on the treatment conditions employed before the HCl treatment step.

$$Fe + 2HCl = FeCl_2 + H_2$$
$$\Delta G_{510^\circ C} = -11.2\,\text{kcal/mol} \tag{3}$$

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$
$$\Delta G_{510^\circ C} = +31\,\text{kcal/mol} \tag{4}$$

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O$$
$$\Delta G_{510^\circ C} = +27.3\,\text{kcal/mol} \tag{5}$$

$$Fe_3O_4 + 2HCl = FeCl_2 + Fe_2O_3 + H_2O$$
$$\Delta G_{510^\circ C} = -3.7\,\text{kcal/mol} \tag{6}$$

Reduced iron readily reacts with HCl according to reaction (3). Reaction between Fe_2O_3 and HCl according to reaction (4) requires very low concentration of water. When the concentration of HCl in the treatment gas is 1% and the reaction pressure is one atmosphere, the estimated equilibrium water concentration is 0.13 ppm. Similarly the equilibrium water concentration for reaction (5) at 1 vol% HCl is estimated to be 1.3 ppm. Therefore, reaction (4) and (5) do not take place to any significant extent during dry HCl treatment of iron oxides coated extrudates (water is generated from reaction of HCl with the hydroxyl groups

Table 3
Reaction of HCl with Fe_3O_4[a]

Run #	Iron crystalline phase after 350°C 6% H_2 + 2% H_2O	0.8% HCl treatment at 510°C	Iron crystalline phase after HCl treatment	wt.% Fe on cat after sonic cleaning
9	$Fe_3O_4/Fe_3O_4/Fe_3O_4$	dry	Fe_2O_3 MFe_2O_3 MFe_3O_4 / MFe_3O_4 MFe_2O_3	0.83/0.54/0.32
10	$Fe_3O_4/Fe_3O_4/Fe_3O_4$	2% H_2O	MFe_3O_4 MFe_2O_3 / Fe_3O_4 / Fe_3O_4	0.62/0.29/0.29

[a] Catalyst loading: $CatFe_2O_3/CatFe_2O_3/CatFe_2O_3$ M = Major phase, m = minor phase

in Al_2O_3). However, Fe_3O_4 may react with HCl according to reaction (6). The equilibrium water concentration for reaction (6) at 1% HCl is estimated to be 0.11 vol%. In a dry HCl treatment, water level in the catalyst bed can be substantially below 0.11 vol% after the HCl front passes by and therefore, reaction (6) shifts toward the right.

Run 9 in Table 3 is a demonstration of reaction (6). Fe_2O_3 was used as the starting material. Transformation of Fe_2O_3 to Fe_3O_4 was attained by a wet hydrogen (6% H2 + 2% H_2O) reduction at 350°C, Fig. 3A (detailed discussion in the relationship of the iron crystalline phase with reduction condition is in the next section). The catalyst was heated up to the HCl treatment temperature, 510°C, in wet helium to maintain the iron particles in the Fe_3O_4 phase. Then the reactor was purge with dry helium. The catalyst was treated with dry HCl at 0.80 vol%. The X-ray diffraction spectra of the catalyst sections after the dry HCl treatment are shown in Fig. 3B–D. X-ray diffraction indicated that iron particles in the first catalyst section (Fig. 3B) were in the form of Fe_2O_3 (no Fe_3O_4 phase left). This section of catalyst also contained $FeCl_2$ chemically bound to Al_2O_3 since there were 0.83 wt.% Fe on the catalyst extrudates after the extrudates were cleaned sonically to remove Fe_2O_3. This iron content might include 0.1 to 0.2 wt.% physically adhered iron oxide particles (see Section 3.5). Therefore, the true level of $FeCl_2$ was close to 1/3 of the original iron loading as suggested by the stoichiometry of reaction (6). Less Fe_3O_4 was converted to $FeCl_2$ and Fe_2O_3 in the second and third sections as indicated in Fig. 3C and 3D. Correspondingly, the amount of iron transfer was reduced in the second and third catalyst sections, and they were 0.54 and 0.32 wt.% respectively. The decrease in the conversion of Fe_3O_4 along the catalyst bed is probably due to a corresponding increase in water concentration. Water was detected in the exit gas by the GC up to the end of the dry HCl treatment. However, the amount was too small to be determined quantitatively. It was estimated to be below 0.1 vol% at the end of the dry HCl treatment. Water is produced when HCl reacts with Al_2O_3. The initial reaction between HCl and the surface hydroxyl group is very quick. Therefore, HCl moves slowly down the catalyst bed as a distinct front. However, after HCl has broken through the catalyst bed, a much slower reaction between HCl and the surface oxide groups of alumina still occurs resulting in an increasing water concentration along the catalyst bed.

The effect of water in suppressing reaction (6) in the forward direction is demonstrated in Run 10 in Table 3. Water at 2 vol% was added to the treatment gas during the HCl treatment. There was no Fe_2O_3 detected in the X-ray spectra of the catalyst extrudates in the second and third sections. Iron existed as Fe_3O_4. However, Fe_2O_3 was detected in the first catalyst section. It was difficult to control the water concentration at the start of this run. During the initial period of the HCl treatment, water concentration was low. This resulted in an appreciable reaction between Fe_3O_4 and HCl in the first section (HCl front did not reach the second and third catalyst sections during the low water concentration period) resulting in a higher iron content in the first catalyst section. The iron contents of the sonically cleaned catalyst were 0.62, 0.29 and 0.29 wt.% for the first, second and third catalyst sections respectively. As it will be shown later, iron transfer to the catalyst is very small for all three catalyst sections when sufficient amount of water is present in the HCl treatment step. Therefore, unlike Fe_2O_3, Fe_3O_4 reacts with HCl under dry condition forming Fe_2O_3 and $FeCl_2$ and the latter is chemically bound to Al_2O_3 at the place of contact.

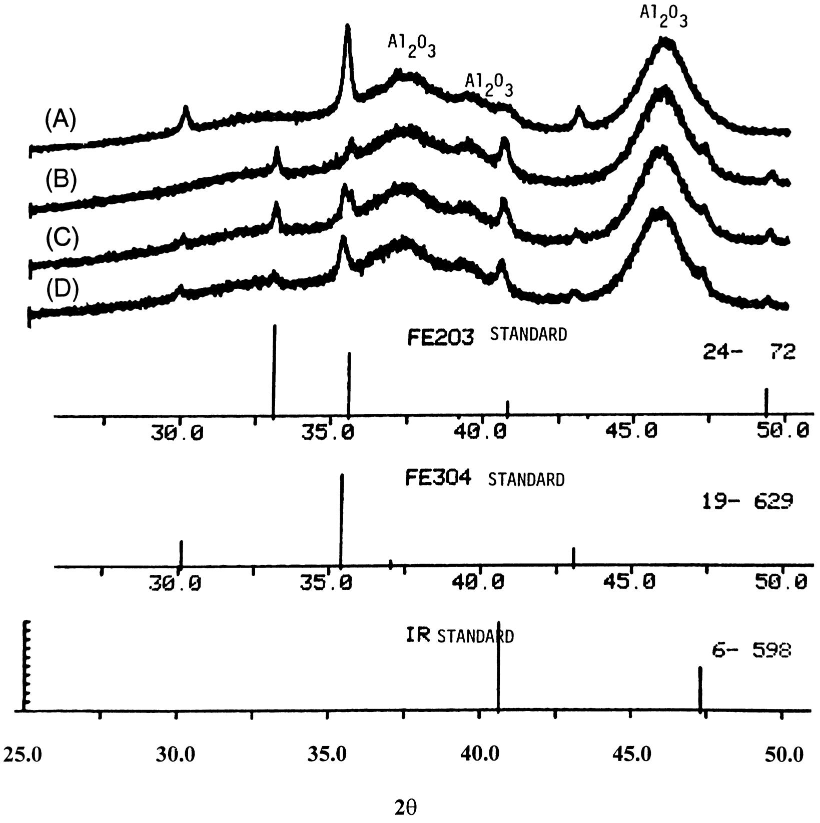

Fig. 3. Reaction of dry 0.8% HCl with Fe_3O_4 fine powder on catalyst extrudates. The Fe_3O_4 was generated by a 350°C, wet hydrogen reduction (6% H_2 + 2% H_2O) of Fe_2O_3 fine powder coated on catalyst extrudates. (A): X-ray spectrum after a wet hydrogen reduction; (B), (C) and (D): X-ray spectra of 1st, 2nd and 3rd catalyst sections respectively, after a wet hydrogen reduction and a dry HCl treatment.

The higher iron transfer experienced by the first catalyst section suggests that the $FeCl_2$ acquired during the initial upset periods (low water) was stabilized by Al_2O_3 and the reverse reaction of reaction (6) was inhibited when water concentration was raised to a higher level at a later time. The inhibition effect of H_2O on the forward direction of reaction (6) is not due to equilibrium limitation, since the strong interaction between Al_2O_3 and $FeCl_2$ shifts reaction (6) to the right even if water is present. It is most probably due to the formation of an inert surface species on the Fe_3O_4 particles but not to the formation of a bulk Fe_2O_3 phase when water concentration is higher than 1 vol% since steam treatment of Fe_3O_4 particles does not transform them to Fe_2O_3 particles. However, the inert surface species may have the composition of Fe_2O_3.

3.7. Oxidation and reduction property of iron

3.7.1. Oxidation of metallic iron by oxygen

The previous section indicates that in order to minimize iron transfer during Pt-Ir catalyst redispersion, the finely divided iron particles which make contact with the catalyst extrudates must be in an oxide form before the HCl treatment step. However, during an on-oil operation iron scale in the reactor are reduced to metallic iron. In the regeneration of Ir containing catalysts, relatively low temperature and low oxygen concentration are employed in the coke burn step to minimize iridium agglomeration. Under this condition, is it possible to convert iron to the oxide phases? Run 11 in Table 4 provides answers to this question.

In addition to the three sections of Pt-Ir catalyst extrudates coated with Fe_2O_3 fine powder, there were

Table 4
Oxidation and reduction of iron

Run #[a]	247°C 2%H_2	450–500°C 2% H_2	Iron crystalline phase after H_2	Iron oxidation condition	Iron crystalline phase in catalyst sections after oxidation
11		Yes	Fe/Fe/Fe/Fe/Fe	430°C 1.2% O_2	FeFilings: MFe, m(Fe_2O_3,Fe_3O_4) All others Fe_2O_3
12		Yes	Fe/Fe/Fe/Fe/Fe	510°C 3.4% H_2O	FeFilings: MFe_3O_4, mFe All others Fe_3O_4
13	Yes		MFe_2O_3 MFe_3O_4 / Fe_2O_3 / Fe_2O_3 / Fe_2O_3		

[a] Catalyst loading for Run 11 and 12: Fe_2O_3/FeFilings/CatFe_2O_3/ CatFe_2O_3/CatFe_2O_3 Catalyst loading for Run 13: Fe_2O_3/CatFe_2O_3/ CatFe_2O_3/ CatFe_2O_3 M = Major phase, m = Minor phase.

packed beds of iron upstream of the catalyst bed. The upstream beds were 0.41 g Fe_2O_3 fine powder followed by 0.53 g iron filings. The samples were reduced with hydrogen at 500°C to simulate the reducing condition of the on-oil operation. After purging out hydrogen, the samples were exposed to 1.2% O_2 (1.22 kPa partial pressure of O_2 usually used in a commercial unit during the coke burn step) at 430°C for 5 h. The discharged catalyst sections and the iron beds were analyzed by X-ray diffraction. The small metallic iron particles in the inlet bed formed by hydrogen reduction of the fine Fe_2O_3 powder, was bulk reoxidized to Fe_2O_3. There was no metallic iron detected in its X-ray diffraction pattern. The particles were non-magnetic. On the other hand the larger iron particles in the iron filing bed exhibited metallic iron as the major phase and a minor oxide phase containing Fe_2O_3 and a smaller amount of Fe_3O_4. The major portion of the particles in this bed is still magnetic. It appears that the larger particle size in the iron filings prevented oxidation of the entire metallic iron particle because the low rate of reaction due to the lower surface area of large iron particles. The fine iron particles (generated from Fe_2O_3 fine powder after hydrogen reduction) in the three catalyst sections can also be bulk oxidized to Fe_2O_3 at the low temperature and low oxygen partial pressure coke burn step.

The inability of the low temperature coke burn step to completely convert iron filing particles to their oxide phase should lead to high iron transfer in the HCl treatment step. However, at the 1 wt.% loading (Run 7, second catalyst section), we observed very little iron transfer, 0.21% Fe, because of very little contact (a small number of iron particles) between iron particles and catalyst extrudates. If a massive amount of iron scale is mixed with the catalyst, high iron transfer can be expected. Therefore, it is advisable to prevent the build-up of iron scale in the reactor by periodic dumping and screening of the catalyst extrudates.

3.7.2. Oxidation of metallic iron by steam

Coke burn temperature used with Ir containing catalyst is generally limited to low temperature in order to minimize iridium agglomeration. Complete conversion of metallic iron scale, especially the large iron particles, to iron oxides at the low coke-burn temperature is not possible. We want to explore ways to use higher temperatures to oxidize iron and maintain iridium in its reduce state. Thermodynamic data indicate that oxidation of metallic iron to Fe_3O_4 and Fe_2O_3 with steam at high temperature is feasible and the formation of IrO_2 agglomerate is impossible. The free energy of the steam–iron reactions as written are:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$
$$\Delta G_{410^\circ C} = -8\,\text{kcal/mol};$$
$$\Delta G_{510^\circ C} = -6\,\text{kcal/mol} \tag{7}$$

$$2Fe + 3H_2O = Fe_2O_3 + 3H_2$$
$$\Delta G_{410^\circ C} = 0\,\text{kcal/mol};$$
$$\Delta G_{510^\circ C} = +1.5\,\text{kcal/mol} \tag{8}$$

The above reactions were studied in Run 12 (Table 4). Catalyst loading configuration was the same as Run 11. The treatment involved a hydrogen reduction at 450°C and a steam treatment up to 510°C for 3 h. Water content in the treatment gas was 3.4 vol%.

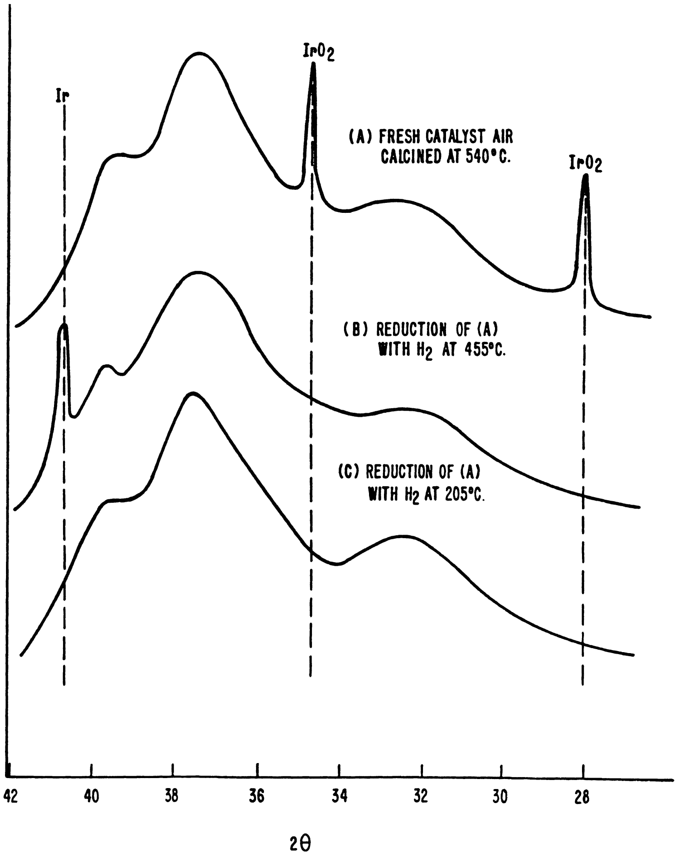

Fig. 4. X-ray spectra of agglomerated iridium on 0.3%Pt-0.3%Ir/γ-Al_2O_3. (A): After the fresh catalyst was air calcined at 530°C for 16 h, (B): After (A) was reduced in hydrogen at 455°C, (C): After (A) was reduced with hydrogen at 205°C.

During the steam treatment, hydrogen was detected at the exit. X-ray diffraction indicated the iron compound in the various sections of the bed was Fe_3O_4, and there was no Fe_2O_3 present. One interesting observation was the near complete conversion of the metallic iron filings to Fe_3O_4. This suggested that the much better reaction kinetics for steam-iron reaction is due to a higher reaction temperature (510°C vs. 430°C) and may be a faster diffusion of H_2O through the Fe_3O_4 phase than O_2 through the Fe_2O_3 phase.

3.7.3. Hydrogen reduction of Fe_2O_3

As mentioned in Section 2, the 100% agglomerated Ir metal standard was produced by hydrogen reduction of a 100% agglomerated IrO_2 standard at temperatures >450°C (Fig. 4A and B, the broad peaks belong to γ-Al_2O_3). However, iridium oxide can be reduced at lower temperatures [10]. Complete reduction of IrO_2 is obtained at temperature as low as 200°C. After the 200°C reduction, the X-ray diffraction pattern shows no iridium peak, i.e., no IrO_2 or Ir metal peaks (Fig. 4C). It appears that the IrO_2 agglomerates are reduced yielding Ir metal particles amorphous to X-ray [13]. However, if after the 200°C reduction, the catalyst is then exposed to a temperature >300°C, Ir metal peaks reappear in the X-ray diffraction pattern (similar to Fig. 4B). It is possible that at 200°C the nucleation of Ir metal centers is fast and the crystal growth process is slow and therefore, many small Ir particles (<50 A), which have close contact with each other, are formed from one large IrO_2 particle and therefore exhibit no distinct X-ray peaks. When these small Ir particles are exposed to higher temperatures they grow easily to a large Ir particle because of their proximity to each other.

The reduction properties of Fe_2O_3 and Fe_3O_4 were investigated with the following catalyst loading configuration: a packed bed of Fe_2O_3 fine powder upstream of the three catalyst sections coated with Fe_2O_3 fine powder. Compared to IrO_2, reduction of Fe_2O_3 and Fe_3O_4 to metallic iron requires more severe conditions. This is mostly due to kinetic limitations. Based on thermodynamic considerations, at 250°C, Fe_2O_3 is in equilibrium with metallic iron when the H_2O/H_2 ratio in the treatment gas is 0.236. However, Run 13 in Table 4 indicated that the Fe_2O_3 fine powder bed remained mostly as Fe_2O_3 with a small amount of Fe_3O_4 but no metallic iron after a dry hydrogen (2 vol%) reduction at 247°C where $H_2O/H_2 << 0.236$. Fe_2O_3 in the three catalyst sections showed no sign of reduction.

Increasing the reduction temperature to 350°C converted the Fe_2O_3 bed to Fe_3O_4 and a small amount of metallic iron. Fe_2O_3 in the three catalyst sections mostly converted to Fe_3O_4 with a small amount of Fe_2O_3 remaining. Maintaining the reduction temperature at 350°C but increasing the concentration of hydrogen from 2 to 6 vol% resulted in more metallic iron in the Fe_2O_3 fine powder bed. However, no metallic iron was detected in the catalyst sections. Addition of 5.4 vol% of H_2O in the 6 vol% H_2 treatment gas inhibits metallic iron formation in the Fe_2O_3 fine powder bed at 350°C and the conversion of Fe_2O_3 to Fe_3O_4 was incomplete. But there was no discernible effect on the iron powder in the three catalyst sections. It remained as Fe_3O_4.

4. Inhibition of iron transfer and maximizing iridium redispersion

4.1. Low temperature reduction keeps iron in Fe_2O_3 phase and Ir in metallic phase

It has been established in the previous section that fine iron powder on the catalyst extrudates can be completely oxidized to Fe_2O_3 after the low temperature coke burn step. An obvious way to avoid iron transfer during redispersion is to skip the reduction step before the HCl saturation. However, IrO_2 agglomerates and oxide layers on the surface of large Ir agglomerates might form even at the low coke burn temperature. Run 14 and 15 in Table 5 show the benefit of low temperature reduction in improving iridium redispersion and still maintaining low iron transfer. The Fe_2O_3 coated catalyst extrudates (100% of its iridium were agglomerated) were first reduced at 500°C to simulate the reduction condition of on-oil operation. Next the catalyst extrudates were treated with 11% O_2 at 430°C for 5 h to simulate the low temperature coke burn. After this operation the crystalline phase of iron on the extrudates was in the form of Fe_2O_3 and the agglomerated Ir metal particles may acquire some oxide layers. Table 5 shows that redispersion is more effective when the low temperature coke burn catalyst was reduced at 280°C at which iridium oxide layers are removed from the iridium agglomerates and iron remained as Fe_2O_3.

4.2. When iron is in Fe_3O_4 phase, water is needed in the HCl treatment step

As mentioned previously, increasing the reduction temperature to 340°C converts the Fe_2O_3 fine powder to Fe_3O_4 and one can also generate Fe_3O_4 from metallic iron if the metallic iron is exposed to steam at 510°C. When iron is in the form of Fe_3O_4, water is needed in the HCl treatment step to inhibit iron transfer.

The advantages of using high temperature reduction and high temperature steam treatment are: it allows all steps, after the low temperature coke burn step, to be carried out at the same temperature and when there are large iron particles high temperature steam treatment completely convert large iron particles to Fe_3O_4 and maintains iridium as metallic iridium. The reduction step was carried out at 510°C in Run 16. After the purging out of hydrogen, water at 2 vol% was introduced to the reactor. Hydrogen was detected at the reactor exit indicating iron was oxidized to Fe_3O_4. This was carried out for 2.5 h to assure complete conversion of iron to Fe_3O_4 before the addition of $HCl + H_2O$. In the subsequent $HCl + O_2$ redispersion step, water was removed from the feed gas. In Table 5, the degree of iridium redispersion and the level of iron transfer of this run are compared with the all wet (2% water) redispersion treatment, Run 17. Both show very little iron transfer. However, an improvement in iridium

Table 5
Redispersion procedures minimize iron transfer and maximize Ir redispersion without elemental chlorine

Run #[a]	6% H_2 reduction	Iron reoxidation	Iron crystalline phase before HCl + O_2	0.4–0.5% HCl + 1.5% O_2	Wt.% Fe on cat after sonic cleaning	Average % residual Ir agglomeration
14	None	None	Fe_2O_3	No H_2O	0.40/0.22/0.19	18
15	280°C	None	Fe_2O_3	No H_2O	0.29/0.19/0.16	9
16	510°C	510°C, 2% H_2O	Fe_3O_4	No H_2O	0.22/0.24/0.22	8
17	510°C	510°C, 2% H_2O	Fe_3O_4	2% H_2O	0.25/0.28/0.21	13

[a] Catalyst loading for Run 14–17: $CatFe_2O_3/CatFe_2O_3/CatFe_2O_3$. This corresponds to the type of iron compounds existed on the catalyst extrudates after the 430°C coke burn step. The catalyst is treated with 0.3% HCl + 2% H_2O to saturation before the HCl + O_2 treatment.

redispersion is observed with Run 16 when the HCl + O_2 step was carried out dry. Since O_2 is present in the redispersion step (HCl + O_2), water is not needed to inhibit iron transfer. Water in the redispersion step reduces the equilibrium chlorine concentration as indicated by reaction C in Fig. 1B. This is why the dry HCl + O_2 redispersion is more effective than when water is present.

5. Conclusions

Understanding of the redispersion chemistry allows us to identify the critical nature in the timing of oxygen exposure during the redispersion of iridium containing catalysts. When the catalyst chloride content is low, e.g., 0.60 wt.%, oxygen exposure at high temperature results in IrO_2 agglomerates and oxide layers on Ir metal agglomerates. They inhibit the redispersion process. In contrast, when the catalyst chloride content is high, e.g., 1.9 wt.%, oxygen can be used with low concentration chlorine containing compounds such as HCl to generate elemental chlorine in situ to completely redisperse Ir agglomerates in one redispersion cycle. This study is the first successful use of non-elemental chlorine to redisperse agglomerated Ir particles.

Iron contamination in iridium containing catalysts after catalyst redispersion is due to transfer of iron through particle contact between catalyst extrudates and iron particles already present in the catalyst bed prior to the redispersion treatment. The critical steps leading to iron transfer are hydrogen reduction and HCl saturation. During the HCl saturation, metallic iron and Fe_3O_4 reacts with HCl to form mobile divalent iron chloride species, which are transferred to the catalyst extrudates at the points of contact. Based on the reaction chemistry between iron, iron oxides and O_2, H_2 and HCl we have devised effective procedures to minimize iron transfer and maximize iridium redispersion. The above reaction chemistry also explains why in certain situations, iron contamination occurs with non-iridium containing noble metal catalysts during catalyst rejuvenation when HCl and iron compounds, with an oxidation state lower than Fe_2O_3, are present.

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