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Trace carbon monoxide and hydrogen conversion prior to cryogenic distillation of air

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Abstract Liquid Nitrogen is required in the semiconductor industry. This is generally produced by cryogenic distillation of air. However, trace levels of Carbon Monoxide and Hydrogen need to be removed from Nitrogen prior to its use in the semiconductor industry. This may be accomplished by catalytic conversion of trace Carbon Monoxide and Hydrogen to Carbon dioxide and Water, respectively. These impurities (Carbon dioxide and Water) are then removed by adsorption from air. The latest technology is to incorporate the catalytic conversion into adsorption based thermal swing pre-purification units, which are already used to remove Water and Carbon dioxide from air prior to its cryogenic distillation. Our experiments show that even though Hydrogen is converted to Water by a catalytic reaction, presence of Carbon dioxide in this stream significantly lowers the performance of the catalyst by as much as five-fold. Also, Hydrogen removal by the novel metal Pd catalyst does not follow a typical catalyst behavior but an adsorption breakthrough type behavior, i.e. for a constant inlet concentration the outlet concentration of Hydrogen breaks through at some time and then increases with time. On the other hand, Carbon monoxide conversion on a Hopcalite type catalyst follows typical catalyst behavior, i.e. for a constant inlet concentration the outlet concentration of Carbon monoxide is constant and does not change with time. Experimental data demonstrating these effects followed by a theoretical explanation are presented.

Keywords Adsorption · Catalysis · Air-purification · Trace removal · Carbon monoxide · Hydrogen

Introduction

Nitrogen is an industrial gas used as a commodity chemical in many applications. Some of these applications include producing an inert atmosphere. Others include chemical production. Still others include Nitrogen used to pressurize Oil wells for Enhanced Oil recovery. Another use is in the manufacture of semiconductor chips. Industrial gas companies have developed many processes to produce Nitrogen from ambient air. The choice of the production method depends upon the amount of gas required and the purity of the final gas product.

One method is pressure swing adsorption (PSA) where air is compressed and sent into a vessel containing Carbon molecular sieve (CMS). This adsorbent preferentially adsorbs Oxygen molecules on to its surface. The effluent during the feed step, produced at feed pressure is Nitrogen. Another adsorption based process uses a molecular sieve Zeolite which preferentially adsorbs Nitrogen. The adsorbed gas is evacuated during

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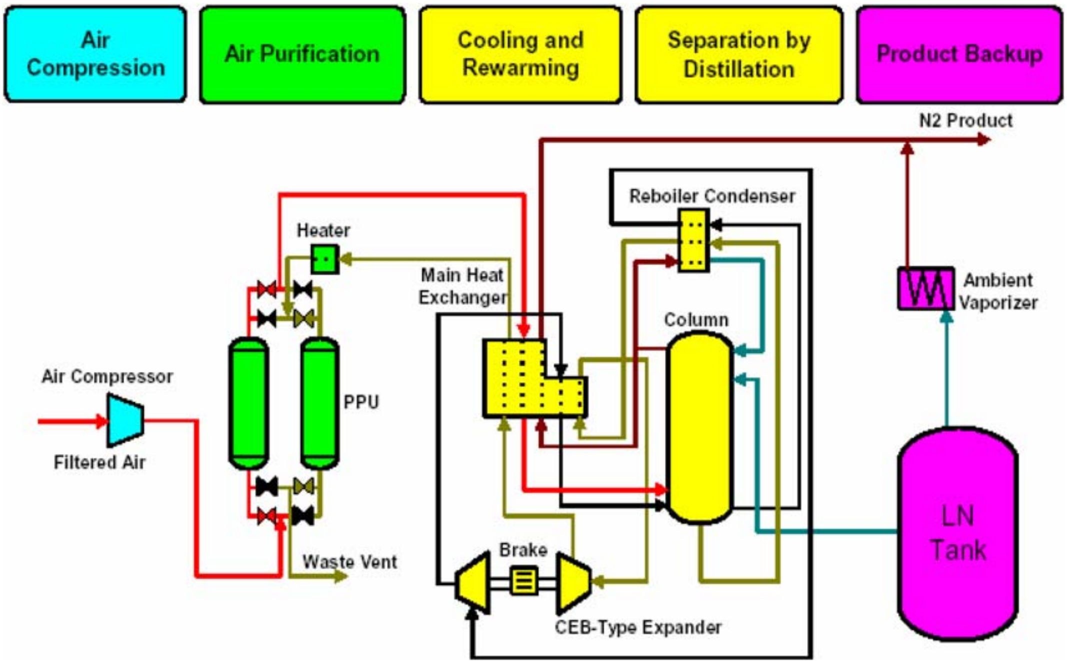

Fig. 1 Typical air separation plant

the regeneration step. The evacuated gas in this vacuum swing adsorption (VSA) process, produced at ambient pressure is primarily Nitrogen with ambient moisture and Carbon dioxide.

An alternative method involves the use of micro porous membranes that have much greater permeability for Oxygen, moisture and Carbon dioxide than for Nitrogen. Oxygen passes through the membrane allowing Nitrogen to exit at the end of the membrane tube at the feed pressure.

All of these processes have their limitations and correspondingly niche market applications. The above mentioned processes are economical only at low production flow rates of Nitrogen (<700 NCMH). From purity—economics trade off point of view, adsorption based processes are competitive upto ∼99.9% Nitrogen purity and, membrane based processes are competitive upto ∼99% Nitrogen purity.

Due to these limitations, cryogenic distillation of air remains the dominant technology for Nitrogen production. Cryogenic distillation can produce very high purity Nitrogen (<10 ppb Oxygen) in liquid form. This Nitrogen may be shipped over the road by trucks, rail road cars or sent to the customer site via a pipe line. Very large cryogenic plants, upto ∼300,000 NCMH Nitrogen, have been built. Efforts are always underway to increase the size range of the cryogenic distillation plants. A typical cryogenic distillation plant to fractionate air is shown in Fig. 1.

Moisture and Carbon dioxide, from ambient air, have to be removed prior to its cryogenic distillation otherwise, these trace impurities tend to freeze and plug up the cryogenic plant. Use of adsorption based processes for this purification has become almost universal (Air Purification "PPU" section in Fig. 1). Recently pressure swing pre-purification adsorption (PSA) processes have gained acceptance in the industry and therefore a larger share of this market (Kumar, 1987). PSA pre-purification is always more economical if the operating conditions are favorable. In this process, air is fed to an adsorbent bed at high pressure. Effluent from this step, at feed pressure, is clean dry air. It is fed to the cryogenic distillation plant. Once the PSA – PPU adsorbent bed is saturated with the contaminants, its pressure is reduced. The saturated adsorbent is regenerated by purge with the waste gas from the cryogenic distillation plant. The applicability of PSA pre-purification technology therefore, is restricted by the availability of the waste gas for the regeneration of the beds. On average ∼50% of the feed air should be available for regeneration. This has restricted the use of PSA pre-purification technology to <80,000 NCMH

Table 1 Air specification for semiconductor industry contaminants in ambient and purified air

	Ambient air	Purified air
H_2O	3000 ppmv	<100 ppbv
CO_2	400 ppmv	<10 ppbv
H_2	0.5–3 ppmv	<1 ppbv
CO	0.5–5 ppmv	<1 ppbv
HCs	1–5 ppmv	ppbv level
N_2O	0.3 ppmv	ppbv level
SO_x/NO_x	ppm level	ppbv level

Nitrogen equivalent plants. The other adsorption technology for air pre-purification, prior to cryogenic distillation, is thermal swing adsorption (TSA) process. In this technology, the adsorbent is regenerated by hot purge gas rather than ambient temperature purge gas as in PSA PPU. The amount of purge gas needed may be as low as ~10% of the feed air. Due to this advantage, TSA is the technology of choice for air pre-purification in large plants, where product recovery is critical. Also, for smaller plants with high Nitrogen recovery (i.e. lower quantity of waste gas available for regeneration) TSA is the technology of choice for air pre-purification prior to cryogenic distillation of air.

Semiconductor industry requires ultra high purity Nitrogen for the manufacture of integrated circuits to prevent defects in the chips of high line densities. In addition to the commonly known impurities from ambient air (Moisture, Hydrocarbons, Carbon dioxide etc.) very stringent requirements are placed on Hydrogen and Carbon monoxide. Typical Nitrogen specifications required by the semiconductor industry are listed in Table 1. Even though air has very low levels of Hydrogen and Carbon monoxide, cryogenic distillation does not remove these impurities and almost all the Hydrogen and about 2/3rd of Carbon monoxide present in ambient air ends up in Nitrogen produced by cryogenic distillation. This is unacceptable to the semiconductor industry.

Stand-alone processes to remove Carbon monoxide and Hydrogen from liquid Nitrogen are suggested in the literature (Daniel, 1996; Hsiung and Wallace, 1999). Also, two-step processes are outlined (Daniel and Bao 1997; Hsiung et al., 2000) in the literature. In the first step of the two step process, feed air is compressed and heated to temperature between 150°C and 250°C. The hot, high pressure air is contacted with a noble metal catalyst to oxidize Carbon monoxide to Carbon dioxide and Hydrogen to moisture. In the second step, the oxidation products from the first step, Carbon dioxide and moisture are removed from the compressed gas stream by temperature or pressure swing adsorption pre-purification process. However, a significant cost saving may be realized (Golden et al., 2000; Jain, 1992; Saxena et al., 2003) if Carbon monoxide and Hydrogen are removed in the pre-purification unit from air prior to its cryogenic distillation. This eliminates separate vessels and corresponding hardware reducing the capital cost and improving operability and reliability.

In this study, we will examine another technology to economically remove Carbon monoxide and Hydrogen from ambient air prior to its cryogenic distillation. Two concepts will be described and experimental data comparing these concepts will be provided.

Two concepts for carbon monoxide and hydrogen conversion from ambient air

A typical thermal swing adsorption (TSA) process for the removal of moisture and Carbon dioxide from ambient air has two vessels. These vessels starting from the feed end are generally packed with activated alumina for moisture removal followed by a Zeolite, such as 13X, for Carbon dioxide removal. During the process, the first vessel is fed with ambient air at high pressure. The adsorbents, Activated Alumina and Zeolite, remove moisture and Carbon dioxide, respectively. Clean air from this vessel is fed to the cryogenic distillation column. Once this vessel is saturated with the impurities, air feed is transferred to the second vessel. Pressure in the first vessel is reduced and it is regenerated by hot purge gas generally in direction counter-current to the feed flow. The adsorbent is then cooled generally by the same purge gas without the heat. After regeneration (heating and cooling) the vessel is pressurized and roles of the two vessels are reversed.

In both the concepts investigated here, Hopcalite-type catalyst (CARULITE-300) was used to oxidize Carbon monoxide to Carbon dioxide and Pd/AA catalyst (Engelhard) to oxidize Hydrogen to moisture. In the first concept (Jain, 1992), the adsorbent/catalyst layers were arranged as follows:

- First layer from the feed-end to remove water (Activated Alumina),

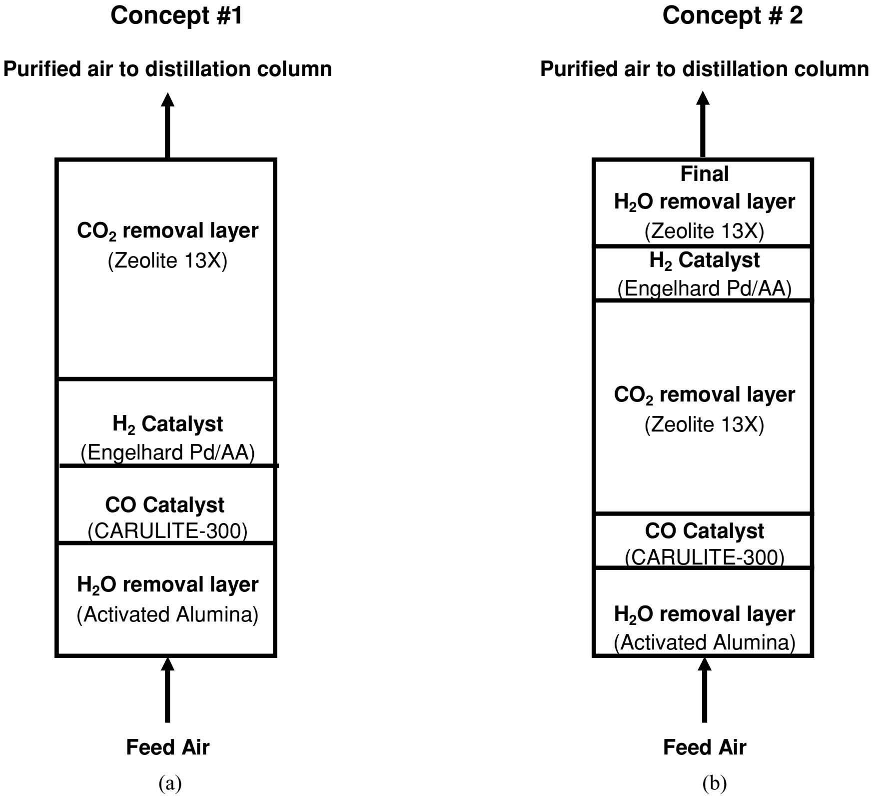

Fig. 2 Layer arrangements for the two Concepts

- Second layer to oxidize Carbon monoxide to Carbon dioxide (CARULITE-300),
- Third layer to oxidize Hydrogen to moisture (Engelhard Pd/AA), and the
- Fourth layer to remove Carbon dioxide present in the ambient feed air, Carbon dioxide generated in the second layer and, water generated in the third layer. This layer could be a Zeolite such as 13X.

This TSA PPU (Pre-Purification) layer arrangement is depicted in Fig. 2(a).

In the second concept (Kumar and Deng, 2003), the adsorbent-catalyst layers were arranged as follows:

- First layer from the feed-end to remove water (Activated Alumina),
- Second layer to oxidize Carbon monoxide to Carbon dioxide (CARULITE-300),
- Third layer to remove Carbon dioxide present in the ambient feed air and Carbon dioxide generated in the second layer (Zeolite 13X),
- Fourth layer to oxidize Hydrogen to moisture (Engelhard Pd/AA), and the
- Fifth and final layer to remove moisture generated in the fourth layer (Zeolite 13X).

This TSA PPU (Pre-Purification) layer arrangement is depicted in Fig. 2(b).

Bench scale experiments

The primary difference between the above mentioned two concepts is the location of Carbon dioxide removal layer (Zeolite 13X). In the first concept (Fig. 2(a)), Carbon dioxide removal layer is located after the Hydrogen conversion catalyst layer whereas, in the second concept (Fig. 2(b)), it is located *before* the Hydrogen conversion catalyst layer. The functional difference in these two concepts therefore, is that in the first concept the Hydrogen conversion catalyst is exposed to ambient level of Carbon dioxide and in the second concept the Hydrogen conversion catalyst is *not* exposed to ambient Carbon dioxide. Therefore, these two concepts may be tested on the same bench unit by turning Carbon dioxide on or off in the feed air. This was done in a small bench unit which is schematically shown in Fig. 3. Adsorbent, Catalyst and vessel details for the

Table 2 Bench scale test unit

Vessel internal diameter = 25.4 mm
Vessel length = 1505 mm
Water removal adsorbent (UOP activated alumina) = 150 mm
CO conversion catalyst (CARULITE 300) = 300 mm
CO conversion catalyst particles = 3.2 mm Pellets
H_2 conversion catalyst (Engelhard Pd/AA) = 150 mm
H_2 conversion catalyst particles = 3.2 mm Beads
Carbon dioxide removal adsorbent (UOP 13X) = 905 mm

bench unit are provided in Table 2. For both of these concepts, Fig. 2(a) and (b), moisture is first removed from the ambient feed air. Therefore, the catalyst layers are not exposed to ambient moisture. In the bench scale test unit, therefore, only moisture free dry air was used. This avoids the complication of introducing wet air to the test unit. Activated alumina adsorbent was packed at the bottom of the bench unit to improve the feed gas distribution and more importantly to line up the sampling lines for both catalysts to appropriate analyzers.

To test the first concept (Fig. 2(a)), the adsorbent and catalysts were first regenerated at 200°C with a dry air stream free of Hydrogen, Carbon monoxide and Carbon dioxide followed by cooling to ambient temperature with the same regeneration gas stream. A dry air feed stream, which contained about 400 ppmv Carbon dioxide, 3128 ppbv Hydrogen and 214 ppbv Carbon monoxide was then introduced to the reactor at 18°C and 12.14 bara from the bottom of the bed. Hydrogen and Carbon monoxide concentrations exiting the Hydrogen conversion catalyst layer were measured by an analyzer (RGA-5) to determine the breakthrough time for both Hydrogen and Carbon monoxide. Carbon dioxide and moisture analyzers were also used to monitor Carbon dioxide and moisture concentrations at the exit end of the Hydrogen conversion catalyst layer and at the vessel exit. Test #1 in Table 3 summarizes the observed performance for the first concept. Carbon monoxide concentration at the out let of the catalyst (CARULTE-300) layer was constant and did not change with time for Test #1, as shown in Fig. 4. This is a normal behavior of a catalyst for oxidizing carbon monoxide. Figure 5 plots the corresponding Hydrogen concentration at the out let of the catalyst (Pd/AA) layer for Test #1. This is not the expected catalyst behavior but adsorption type breakthrough behavior. After the

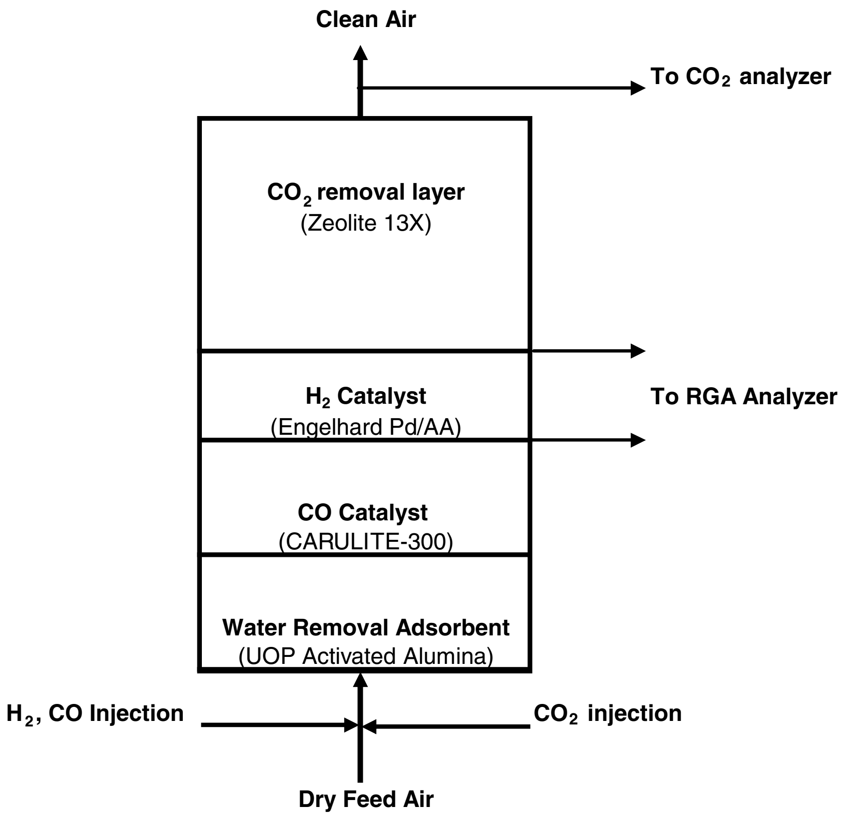

Fig. 3 Bench scale test unit

Table 3 Bench scale test results

	Effect of CO_2 in feed		Effect of feed pressure		Effect of Pd content	
	Test #1$^{(2)}$	Test #2$^{(2)}$	Test #3$^{(3)}$	Test #4$^{(3)}$	Test #5$^{(3)}$	Test #6$^{(3)}$
Feed Pressure, bara	12.14	12.14	11.56	9.18	11.90	11.90
Feed Temperature, °C	18	18	25	25	20	20
Superficial Velocity, mmps	143	143	91	91	91	91
H_2 in Feed, ppbv	3100	3200	3000	3100	1000	1000
CO in Feed, ppbv	210	230	5000	5000		
CO_2 in Feed, ppmv	400	<0.1	400	400	<0.1	<0.1
Pd Content of H_2 conversion Pd/AA Catalyst	0.5%	0.5%	0.5%	0.5%	0.5%	0.3%
H_2 breakthrough Time$^{(1)}$, min	75	400	590	600	1000	600

(1): Defined at 2 ppbv H_2.

(2): Layer arrangement as shown in Fig. 3: Carbon monoxide conversion catalyst (Carulte-300), Hydrogen conversion catalyst (Pd/AA) followed by Carbon dioxide removal adsorbent (13X).

(3): Layer arrangement: Carbon monoxide conversion catalyst (Carulte-300), Carbon dioxide removal adsorbent (13X) followed by Hydrogen conversion catalyst (Pd/AA).

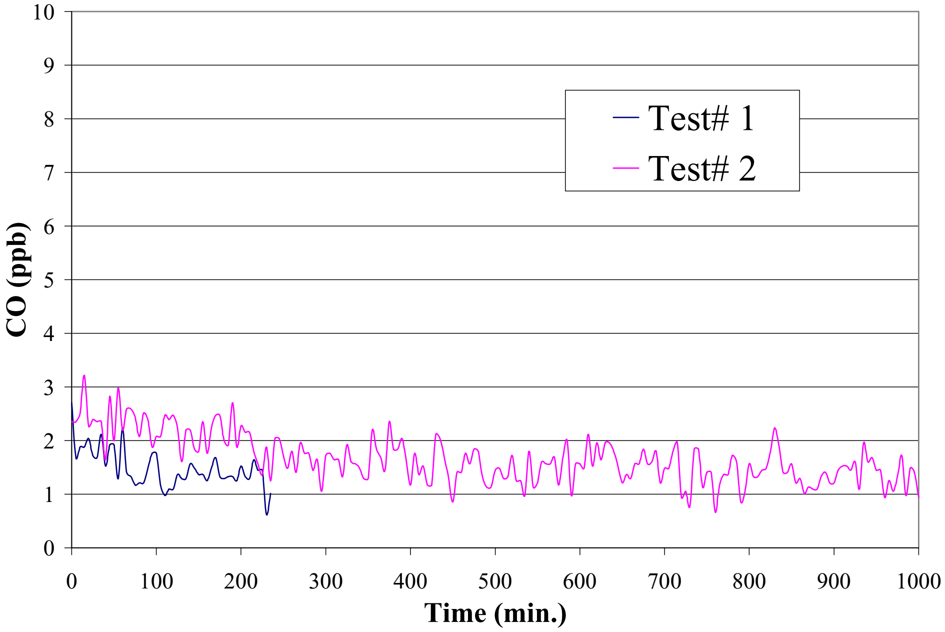

Fig. 4 Carbon monoxide concentration at the outlet of CARULITE 300 from bench tests

adsorbent-catalyst bed was saturated with the impurities, its pressure was reduced to ambient level and the vessel was regenerated at 200°C by flowing dry air stream free of Hydrogen, Carbon monoxide and Carbon dioxide in direction counter-current to the feed flow. This was followed by cooling to ambient temperature with the same regeneration gas stream. The vessel was pressurized and the feed step was restarted.

The second concept (Fig. 2(b)) was also tested on the same bench unit as shown in Fig. 3 with the details listed in Table 2. The adsorbent and catalysts were first regenerated at 200 °C with a dry air stream free of Hydrogen, Carbon monoxide and Carbon dioxide followed by cooling to ambient temperature with the same regeneration gas stream. In contrast to concept #1, the feed air to test this concept did *not* contain any Carbon dioxide. This is a valid test for this concept since Carbon dioxide from ambient air is removed *prior* to its contact with Hydrogen conversion catalyst as explained above and shown by the proposed layer arrangement in Fig. 2(b).

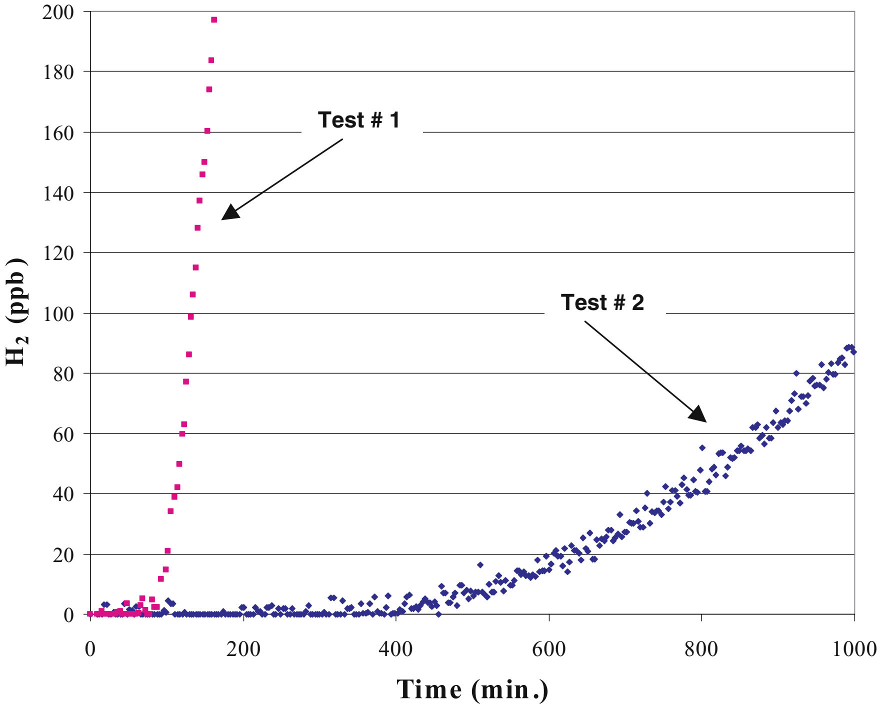

Fig. 5 Hydrogen breakthrough curves from bench tests

A dry air feed stream, which contained *no* Carbon dioxide, about 3286 ppbv Hydrogen and 232 ppbv Carbon monoxide was then introduced to the reactor at 18°C and 12.14 bara from the bottom of the bed to simulate the second concept. Hydrogen and Carbon monoxide concentrations exiting the Hydrogen conversion catalyst layer were measured by an analyzer (RGA-5) to determine the breakthrough time for both Hydrogen and Carbon monoxide. Carbon dioxide and moisture analyzers were also used to monitor Carbon dioxide and moisture concentrations at the exit end of the Hydrogen conversion catalyst layer and at the bed exit. Test #2 in Table 3 summarizes the observed performance for the second concept. Again, Carbon monoxide concentration at the out let of the catalyst (CARULTE-300) layer was constant and did not change with time as shown in Fig. 4. Figure 5 plots the corresponding Hydrogen concentration at the out let of the catalyst (Pd/AA) layer for Test #2. This, again, is not the expected catalyst behavior but adsorption type breakthrough behavior. After the adsorbent-catalyst bed was saturated with the impurities, its pressure was reduced to ambient level and the vessel was regenerated at 200°C by flowing dry air stream free of Hydrogen, Carbon monoxide and Carbon dioxide in direction counter-current to the feed flow. This was followed by cooling to ambient temperature with the same regeneration gas stream. The vessel was pressurized and the feed step was restarted.

As expected from catalytic oxidation reaction theory there was no Carbon monoxide "breakthrough" after the Carbon monoxide (CARULTE – 300) conversion catalyst layers in both the tests. This implies that we had enough Carbon monoxide catalyst in the vessel. However, as shown in Fig. 5, Hydrogen showed a "breakthrough" type behavior from the Pd/AA catalyst layer in both the experiments (Test #1 and Test #2). This looks like a typical adsorption breakthrough type behavior and contradicts the theory for conventional catalytic oxidation of Hydrogen.

Table 3 and Fig. 5, show that Hydrogen breakthrough time extends from 75 minutes to 400 minutes from Test #1 to Test #2. The primary difference between these two tests is that the feed for Test #1 contains ∼400 ppm Carbon dioxide whereas feed for Test #2 *does not* contain any Carbon dioxide except for what is produced by the Carbon monoxide conversion catalyst (230 ppb). This clearly suggests that the performance of Hydrogen conversion catalyst is greatly enhanced (5 time) if there is no Carbon dioxide in the feed stream to the Hydrogen catalyst layer. Based upon these experimental results from the bench unit, the new bed configuration as shown in Fig. 2(b) was tested in

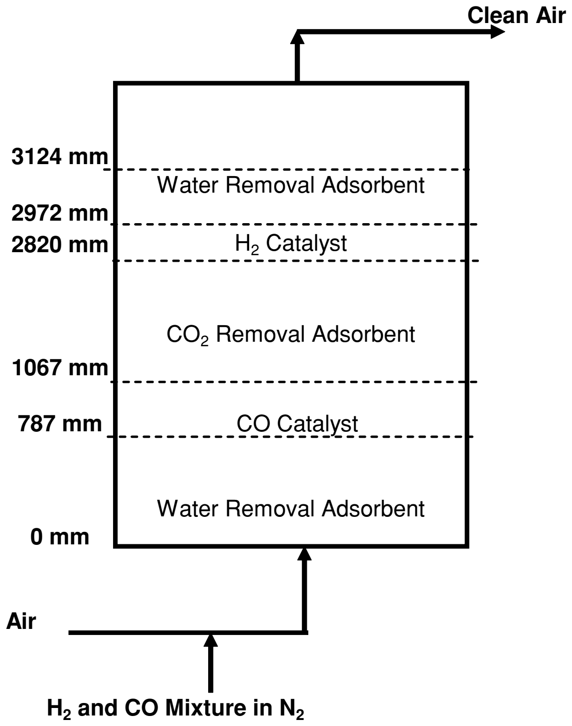

Fig. 6 Large scale test vessel

a large scale air purification plant before the concept was commercialized.

Effect of Feed Pressure

Two experimental runs (Test #3 and Test #4) were conducted on the bench unit to study the effect of feed pressure on the performance of Hydrogen conversion catalyst. For these experiments, the layer arrangement of the bench unit was changed to Carbon monoxide conversion catalyst, Carbon dioxide removal adsorbent (13X) followed by Hydrogen conversion catalyst. In addition, Carbon dioxide was added to the dry air feed stream. The experimental conditions for these two tests were quite similar except that Test #3 was performed at 11.56 bara and Test #4 was carried out at 9.18 bara. The Hydrogen breakthrough time from Test #3 and Test #4, as listed in Table 3, are 590 minutes and 600 minutes, respectively. These values are identical within experimental uncertainties. This suggests that feed air pressure does not affect the performance of the Hydrogen conversion catalyst.

In addition, comparison of Hydrogen breakthrough times from Test #3 and Test #4 with Test #1 in Table 3 further reinforces the conclusion that removal of Carbon dioxide from air prior to contact with the Hydrogen conversion catalyst layer enhances the performance of Hydrogen conversion catalyst significantly.

Effect of Pd content on Hydrogen conversion catalyst (Pd/AA)

Two more experiments (Test #5 and Test #6), as shown in Table 3, were performed to study the effect of Pd content of the Pd/AA catalyst on the performance of Hydrogen conversion catalyst. For these experiments, the layer arrangement of the bench unit was kept same as in Test #s3 and 4 i.e. Carbon monoxide conversion catalyst, Carbon dioxide removal adsorbent (13X) followed by Hydrogen conversion catalyst. However no Carbon monoxide or Carbon dioxide was introduced in the feed. The experimental conditions for these two tests were same except that Test #5 was performed on a catalyst with 0.5% Pd and Test #6 was performed on a catalyst with 0.3% Pd. As shown in Table 3, the Hydrogen breakthrough time obtained on these two catalyst samples is directly proportional to the Pd content of the Pd/AA catalyst.

Large scale experiments

The novel metal based Hydrogen conversion (Pd/AA) catalyst is very expensive. Therefore, once it was demonstrated in the bench unit that removing Carbon dioxide from air prior to its contact with Hydrogen conversion (Pd/AA) catalyst (Fig. 2(b)) rather than, flowing the Carbon dioxide and Hydrogen containing air over the Hydrogen conversion catalyst (Fig. 2(a)), reduces the quantity of Hydrogen conversion (Pd/AA) catalyst five fold, it was decided to test this concept on a larger scale unit. This testing was done on an air-separation plant such as shown in Fig. 1. The two PPU vessels were previously packed with the adsorbent-catalyst arrangement such as shown in Fig. 2(a). This arrangement was changed and the vessels were re-packed with the adsorbent-catalyst arrangement as shown in Fig. 2(b). The two large vessels as packed for these tests are schematically shown in Fig. 6.Adsorbent, catalyst and vessel details are listed in Table 4. The test vessels were instrumented for detailed gas analysis. Hydrogen and Carbon monoxide were mixed in the feed air prior to its entry into the

Table 4 Large scale test vessels

Vessel internal diameter = 1118 mm
Vessel length = 4064 mm
Water removal adsorbent on the feed end (activated alumina) = 590 kg
CO Conversion catalyst (CARULITE 300) = 245 kg
CO Conversion catalyst particles = 3.2 mm Pellets
CO Conversion catalyst, packed density = 897 kg/c. m.
Carbon dioxide removal adsorbent (UOP 13X) = 1179 kg
H_2 Conversion catalyst (Engelhard Pd/AA) = 104 kg
H_2 Conversion catalyst particles = 3.2 mm Beads
H_2 Conversion catalyst, packed density = 689 kg/c. m.
Water removal adsorbent on the product end (UOP 13X) = 100 kg

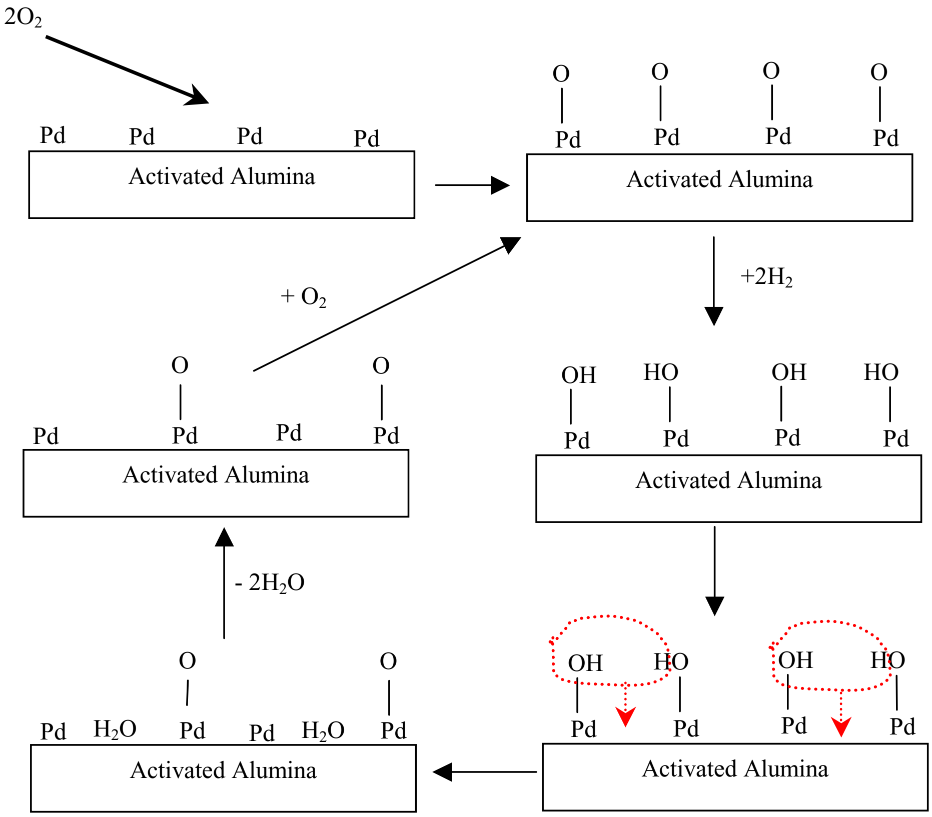

Fig. 7 Schematic diagram showing the surface phenomena involved in H_2 oxidation on Pd active sites

vessel to obtain feed air with desired amounts of impurities to the vessel.

Hydrogen, Carbon monoxide, Carbon dioxide and moisture were monitored, respectively at the exit end of the Hydrogen conversion catalyst layer, Carbon monoxide conversion catalyst layer and at the vessel exit. Hydrogen concentration in the feed air was changed such that Hydrogen was detected first at the exit of the Hydrogen conversion catalyst layer prior to Carbon dioxide or moisture showing up at the vessel exit. Once Hydrogen was detected at the exit of the Hydrogen conversion catalyst layer, feed air was transferred to the other vessel. The first vessel was then depressurized, regenerated by heating the waste gas from the cryogenic air separation unit. It was then cooled, repressurized and put back on the feed step while the second vessel was now depressurized and regenerated.

Table 5 Large scale test results

	Test #A	Test #B
Feed pressure, bara	9.9	9.9
Feed temperature, °F	23	26
Feed flow rate, NCMH(1)	3000	3000
Superficial velocity, mmps	91.5	94.5
H_2 in Feed, ppbv	4400	6100
CO in feed, ppbv	5700	8100
H_2 breakthrough time (2), min	600	430
H_2 breakthrough capacity, μ mole H_2/g Catalyst	12.6	12.2

(1): NCM defined at 1 atm and 0°C.
(2): Defined at 1 ppbv H_2.

Two of the experimental results are reported in Table 5. Again, Carbon monoxide concentration at the out let of the catalyst (CARULTE-300) layer was constant and did not change with time. Hydrogen breakthrough times were significantly longer than for the prior layering arrangement, Fig. 2(a), and were of the similar magnitude as expected from the bench unit data.

Results from Test #A and Test #B show that Hydrogen breakthrough time is approximately inversely proportional to Hydrogen concentration in feed air. Breakthrough capacity for Hydrogen conversion by the Pd/AA catalyst was calculated by the following equation:

$$n = F_f * Y\,\mathrm{H}_2 * t/W$$

where, n is the Hydrogen breakthrough capacity, F_f is the feed flow rate, $Y\,\mathrm{H}_2$ is concentration of Hydrogen in feed, t is the breakthrough time and W is the weight of the Hydrogen conversion catalyst. Hydrogen breakthrough capacity was calculated to be 12 μ mole of Hydrogen per g of the catalyst and is reported for Test #A and Test #B in Table 5.

Theoretical analysis

The breakthrough behavior of H_2 on the Pd/AA catalyst is not expected from the traditional catalytic reaction theories as long as the catalyst dose not deactivate. The effect of CO_2 on H_2 breakthrough time is even more interesting. In order to elucidate the mechanism of H_2 breakthrough behavior on the Pd/AA catalyst and to investigate the CO_2 effect on H_2 oxidation, the Langmuir—Hinshelwood kinetics model was applied to analyze the mass transfer and reaction steps in the oxidation of H_2 on Pd/AA surface.

The Pd/AA catalyst has a typical core and shell type structure, with the majority of the core as activated alumina and a thin shell of metallic palladium. In Pd/AA catalyst the nano-particles of Pd atom clusters are uniformly dispersed on the surface of the mesopores of activated alumina. The H_2 oxidation reaction on Pd/AA surface can be treated as a traditional heterogeneous catalytic reaction. According to Fogler (Fogler, 1999), this catalytic reaction may consist of the following steps:

1. Mass transfer (diffusion) of reactants H_2 and O_2 from gas phase to the external surface of the Pd/AA catalyst,
2. Diffusion of reactants (H_2 and O_2) from the catalyst pore mouth to the immediate vicinity of the internal catalytic surface (Pd clusters);
3. Adsorption (physical or chemical) of reactants onto the surface of the Pd sites;
4. The adsorbed species (H_2 and O_2) react to form product (H_2O) on active Pd sites,
5. Desorption of the product H_2O from the Pd sites,
6. Diffusion of product H_2O from Pd sites to the pore mouth of the external surface, and
7. Mass transfer of the product H_2O from the Pd/AA catalyst external surface to the gas phase.

There is also adsorption equilibrium between the gaseous H_2O molecules and adsorbed H_2O molecules on the internal surface of the activated alumina.

The pore textural properties measured on an activated alumina sample similar to the Pd/AA catalyst support reveal that the median pore size of activated alumina is about 5 nm (Deng and Lin, 1997). It is expected that the main mass transfer mechanism of gases in mesopores of Pd/AA catalysts is Knudsen diffusion. The estimated Knudsen diffusivity of hydrogen in activated alumina at 10 bar and 300 K (typical operating conditions given in Table 3) is 0.03 cm^2/s, which is same order of magnitude as molecular diffusivity of hydrogen in nitrogen (0.07 cm^2/s) at similar conditions (Welty et al., 2001). This strongly suggests that the mass transfer of gaseous reactants and products in the pores of Pd/AA catalyst is not the rate limiting steps.

It is believed that the controlling steps in catalytic reactions on commercial catalysts are usually the surface phenomena that include reactants' adsorption, surface reactions, and product desorption (Fogler, 1999; Masel, 1996; Bielanski and Haber, 1991; Levenspiel, 1972). The following are the proposed reactions for the surface phenomena involved in the H_2 oxidation on Pd/AA catalyst surface. The first two equations represent the chemical adsorption of O_2 and H_2 on the Pd active sites. Equations (3) to (7) are the possible surface reactions on Pd active sites between the adsorbed species and reactants. Equation (8) is desorption of adsorbed H_2O from Pd sites to gas phase:

$$O_2 + 2S \rightarrow 2O_{(a)} \tag{1}$$

$$H_2 + 2S \leftrightarrow 2H_{(a)} \tag{2}$$

$$2O_{(a)} + H_2 \rightarrow 2OH_{(a)} \tag{3}$$

$$O_{(a)} + H_2 \rightarrow OH_{(a)} + H_{(a)} \tag{4}$$

$$O_{(a)} + H_{(a)} \rightarrow OH_{(a)} \tag{5}$$

$$2OH_{(a)} \rightarrow H_2O_{(a)} + O_{(a)} \tag{6}$$

$$H_{(a)} + OH_{(a)} \rightarrow H_2O_{(a)} \tag{7}$$

$$H_2O_{(a)} \rightarrow H_2O_{(a)} + S \tag{8}$$

Figure 7 is a schematic diagram showing the H_2 oxidation surface phenomena when the O_2 concentration in the gas phase is much greater than H_2, which is the typical case in the ambient air purification where H_2 concentration is in parts per million while oxygen molar concentration is more than 20%. O_2 is first adsorbed on vacant Pd active sites to form the adsorbed oxygen following Eq. (1), the adsorbed Oxygen then reacts with molecular Hydrogen (H_2) in the vicinity of the adsorbed Oxygen site to form adsorbed OH groups following reaction (3). This leads to the conversion of molecular Hydrogen from the gas phase. The adsorbed OH groups forms water molecules and desorbes from the active Pd sites following reactions (6) and (7), desorption of Water molecules replenishes the active Pd sites for the next cycle of Hydrogen oxidation reaction. If each step of the surface phenomena (O_2 adsorption, surface reaction and H_2O desorption) as described in Fig. 7 has similar rate of reaction, the catalytic process will continue without interruption, and Hydrogen will be continually removed from the gas phase as long as the catalyst is active, Hydrogen breakthrough should not occur in the air purification process investigated in this work.

Feed air without CO_2

However, H_2 breakthrough did happen in air purification processes with and without Carbon dioxide (Fig. 5) in the feed air. Let us first consider the case of using feed air without Carbon dioxide. According to Levenspiel (Levenspiel, 1972), if H_2O desorption is the rate-limiting step in the H_2 oxidation process described in Fig. 7, the overall H_2 oxidation rate is independent of feed pressure, i.e. the H_2 conversion efficiency is not a function of feed pressure. It was observed in our lab studies, as shown in Table 3, that the feed air pressure does not affect the Hydrogen conversion efficiency. This allows us to conclude that desorption of H_2O from the active Pd site is the rate-limiting step in H_2 oxidation on Pd/AA catalyst. This is probably due to the fact that activated alumina used in Pd/AA catalyst support is hydrophilic and excellent water adsorbent even at low water concentrations. The water molecules formed on the active Pd could stay in the vicinity of Pd site and flood the Pd sites eventually. This hypothesis can be validated either by a simple thermal gravimetric analysis (TGA) of a spent Pd/AA catalyst to prove the increase of water molecules around Pd sites, or by H_2 oxidation experiments with Pd catalyst on a hydrophobic support such as activated carbon or high silica to alumina ratio Zeolites. It is speculated that H_2 oxidation on such a new Pd catalyst will follow the conventional oxidation reaction without H_2 breakthrough type behavior.

If water desorption is the rate-limiting step in the in H_2 oxidation on Pd/AA catalyst, the slower desorption of H_2O will slowly deplete the active Pd sites, adsorbed H_2O molecules on AA support will slowly cover the Pd active sites, and the H_2 oxidation will

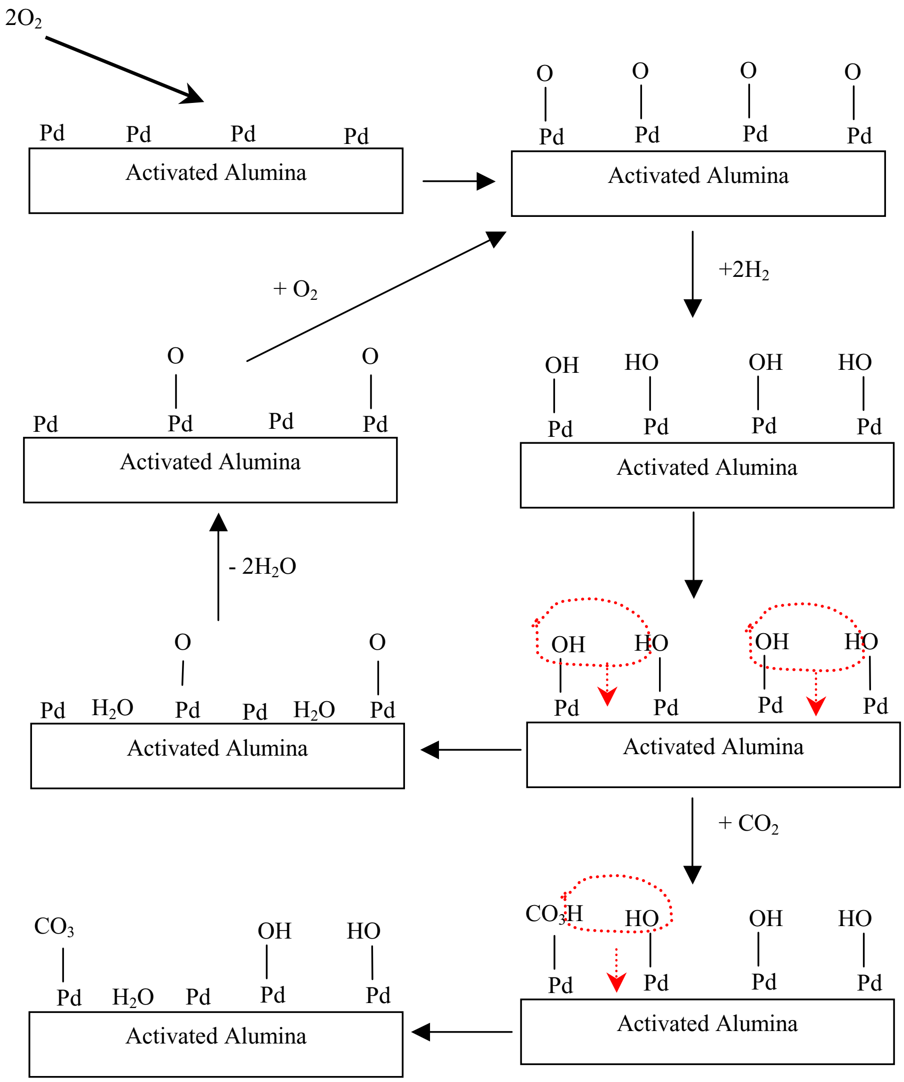

Fig. 8 Schematic diagram showing the CO_2 effect on H_2 oxidation on Pd active sites

behave like an adsorption process. In such a case, the Hydrogen molecules adsorb on the adsorbed oxygen atoms through a chemical adsorption, Hydrogen breakthrough is expected once all the active Pd sites are consumed. In this case the Hydrogen adsorption capacity determined from the breakthrough curve is proportional to the Pd loading on the catalyst, which agrees well with experimental results of Hydrogen conversion with Pd/AA catalysts of different Pd loadings as shown in Table 3. This experimental observation of the effect of Pd loading on H_2 conversion capacity gives us another process parameter to optimize the air purification processes.

Feed air with CO_2

When 400 ppmv CO_2 is present in the feed air as used in the bench scale Test #1 (Table 3), the Hydrogen breakthrough time was shortened by more than 80%. This suggests that CO_2 interferers with H_2 oxidation on Pd/AA catalyst. The concentration ratio of CO_2 to H_2 is about 130. It is speculated that the following reactions occur when CO_2 is present in feed air in the H_2 oxidation process.

$$CO_2 + OH_{(a)} \rightarrow HCO_{3(a)} \tag{9}$$

$$OH_{(a)} + HCO_{3(a)} \rightarrow CO_3(a) + H_2O_{(a)} \tag{10}$$

It is well known from adsorptive air purification processes for CO_2 and H_2O, conversion and the surface chemistry of activated alumina that CO_2 adsorbs strongly on the hydroxyl group (OH) on the activated alumina surface even at low concentrations (Gregg and Ramsay, 1969; Manchado et al., 1994; Parkyns, 1971; Peri, 1966). It is expected that the hydroxyl groups formed on Pd surface will behave similarly to the hydroxyl groups on AA. As shown in Fig. 8, CO_2 adsorbs on the adsorbed OH groups to form the adsorbed HCO_3 groups following reaction (9), this is then decomposed into adsorbed CO_3 group and adsorbed H_2O molecules. The adsorbed CO_3 groups are quite stable and will not desorb unless the temperature is increased, which leads to a much faster depletion rate of the active Pd sites and a faster Hydrogen breakthrough. This assumptions can be verified by FT-IR analysis of used Pd//AA catalyst to identify the adsorbed CO_3 group on the Pd surface (Peri, 1966; Peri and Hannan, 1960).

Conclusions

Based upon the experimental data on the bench unit at these operating conditions:

- Breakthrough type behavior rather than typical catalyst behavior for oxidation of Hydrogen to water on Pd/AA catalyst is observed,
- Breakthrough time of Hydrogen without Carbon dioxide in feed air is five times the breakthrough time of Hydrogen with Carbon dioxide in feed air,
- Breakthrough time is not effected by the total feed air pressure,
- Breakthrough time is directly proportional to Pd content of the Pd/AA catalyst,
- Breakthrough time is inversely proportional to Hydrogen concentration in feed air.

Since the Hydrogen conversion catalyst is a very expensive noble metal catalyst a reduction in its requirement results in significant cost savings even though the new arrangement requires an additional fifth layer.

From the theoretical analysis, It is believed that catalytic conversion of Hydrogen on Pd/AA catalyst is controlled by the rate of water desorption from the catalyst support, and strong adsorption of Carbon dioxide on hydroxyl groups (OH) formed on Pd active sites further accelerates the deterioration of Pd/AA performance.

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