EX-SITU REDUCTION AND DRY PASSIVATION OF NOBLE METAL CATALYSTS

BACKGROUND OF THE INVENTION

[0001] The present invention relates to methods for the ex-situ activation and passivation of catalysts. In particular, these methods relate to supported noble metal catalysts on meso-porous or zeolitic materials. These techniques also apply to all catalyst that absorb water and use supported noble metals.

[0002] In-situ nitrogen drying and hydrogen reduction of noble metal catalysts is sometimes difficult to implement in commercial plants. Catalysts must first be completely dried under inert gas (N_2) and then the water partial pressure must be maintained at extremely low levels during hydrogen reduction to prevent damaging highly dispersed noble metals. Commercial plants have a variety of treat gas compositions and limits on minimum operating pressures and purge gas rates. Therefore, for large catalyst volumes, in-situ activation can last for weeks and the success relies heavily on accurate treat gas dew point measurements, which can be quite unreliable. Also, Nitrogen for drying is not always available and the large volumes needed for adequate drying may be prohibitively expensive to purchase.

[0003] Ex-situ reduction and dry passivation eliminate the need for extensive in-situ treatment. This reduces start-up time and eliminates the potential to damage noble metal dispersion during commercial in-situ reduction in the presence of moisture.

[0004] Currently, most noble metal catalysts are loaded into the reactor with the metal in the oxide form and then the noble metals are activated/reduced in-situ in the commercial unit. As mentioned above, in-situ activations can last for weeks and the presence of excessive moisture during reduction can significantly damage noble metal dispersion. For limited applications, the noble metals are

activated ex-situ and the reduced catalyst is immediately immersed into excess oil, wax or liquids, in an inert atmosphere, to passivate the noble metals. However, catalysts immersed in excess liquid are very difficult to handle and impossible to load into most multi-bed reactors.

SUMMARY OF THE INVENTION

[0005] The present invention is a process for the ex-situ reduction and dry passivation of a supported noble metal catalyst including a mesoporous or zeolitic matrix. The process includes the steps of reducing the catalyst and passivating the catalyst in the absence of excess liquid. In one preferred embodiment, the reduced catalyst is first cooled, in an inert atmosphere, and then exposed to air. In another preferred embodiment, the pores of the reduced catalyst may be filled with oil in an inert atmosphere. Since only the pores are filled with oil, the catalyst remains dry and free flowing.

[0006] In a preferred embodiment, the supported metal catalyst is palladium and platinum supported on MCM-41 bound with alumina, which is described in U.S. 5,098,684.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 shows a comparison of the performance of a palladium and platinum supported catalyst that was reduced in-situ versus ex-situ according to the present invention as in Example 2.

[0008] Figure 2 shows the catalyst performance of Example 4.

[0009] Figure 3 shows the air passivated catalyst performance of Example 4.

[0010] Figure 4 shows the oil pore-filled catalyst performance of Example 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] The present invention is a method of ex-situ activation and dry passivation of supported noble metal catalysts. The method comprises a two step procedure. First, the supported noble metal oxides are first dried and reduced in a single step in the presence of a mixture of hydrogen and inert gas. Second, the reduced catalyst is dry passivated by cooling in an inert atmosphere and then exposing to air or by filling the pores of the catalyst with a ultra low sulfur mineral oil before exposing to air. The passivated catalysts are dry and free flowing and can be easily loaded into a commercial reactor, heated in hydrogen to remove free water & oxygen of passivation, and then started on oil feed, without any further treatment.

[0012] Ex-situ reduction and passivation will reduce start-up time and eliminates the potential to damage noble metal dispersion during in-situ reduction in the presence of moisture. While ex-situ passivation of reduced catalysts in excess oil or wax has been practiced commercially, dry passivation with air or by oil-pore filling is novel and offers the advantage of a free flowing catalyst. Further, pilot plant data show that ex-situ reduced and dry passivated catalysts have equivalent performance as catalysts having been subjected to a controlled in-situ drying and reductions step using completely dry gases. The method described in the examples below is for palladium and platinum supported on MCM-41 bound with alumina.

Example 1: In-Situ Reduction

[0013] The catalyst comprises 0.3 wt% platinum and 0.9 wt% palladium supported on MCM-41 bound with alumina. Platinum and palladium are highly dispersed on the surface of the catalyst support by first absorbing onto the support an aqueous solution of platinum and palladium tetrammine nitrate. After metals coating, the support is dried and then calcined in air to decompose the

tetrammines, leaving behind finely dispersed platinum and palladium oxides. Prior to use, the catalyst must be activated by reducing the platinum and palladium oxides without damaging metal dispersion.

[0014] Current practice is to load such noble metal catalysts into the commercial reactor and first dry the catalyst in nitrogen and then reduce the noble metals in hydrogen. As shown in the Table 1 below, the catalyst must be completely dried in inert gas such as nitrogen prior to reduction and water partial pressure must be maintained at extremely low levels during hydrogen reduction to prevent damaging the dispersion of the noble metals, while the temperature must be at least 150°C to fully reduce the noble metals.

TABLE 1

Effect of Drying Conditions

	Drying		Hydrogen Reduction				Dispersion
	Temp, C	Time, hr	Water, psi	Temp, C	Time, hr	Water, psi	O/M
Successful	85	12	0.09	240	9	0.09	0.60
Insufficient Drying	88	2	6	229	6	0.01	0.26
High P_{H20}	84	22	6	237	10	0.3	0.37

[0015] For some limited applications, the noble metals can be reduced ex-situ and the reduced catalysts immediately immersed into excess oil, wax, or other liquid (in an inert atmosphere) to passivate the noble metals. However, catalysts immersed in excess liquid are very difficult to handle and are only useful for single bed reactors because they are impossible to load into most multi-bed reactors.

Example 2: Ex-Situ Reduction and Passivation

[0016] In ex-situ reduction, the supported noble metal oxides are first dried and reduced in a single step in the presence of a mixture of hydrogen and inert gas in a rotary calciner. As shown in Table 2, oxygen chemisorption results on

the nitrogen blanketed samples following ex-situ reduction in a rotary calciner show that the catalyst was fully reduced with no agglomeration of noble metals.

[0017] The air-passivated catalyst was prepared by cooling the reduced catalyst in nitrogen and then slowly exposing the reduced catalyst to air at room temperature. In this step, oxygen is absorbed onto the catalyst surface preventing oxidation of the reduced noble metals. Oxygen chemisorption measurement (0.01 O/M) shown in Table 2 indicates that the noble metal sites are covered with oxygen. Further, chemisorption experiments also indicate that the oxide coating can be easily removed at very mild conditions (>35°C in hydrogen) to expose fully reduced and highly dispersed, active noble metal sites.

[0018] The oil pore-filled passivated catalyst was prepared, under inert gas (N2), using a oil pore-filled passivation technique. In this case, medicinal grade white oil was added to the reduced catalyst to fill about 95% of the pores volume. Reduced catalyst samples passivated with oil could not be analyzed by oxygen chemisorption.

TABLE 2

Metal Dispersion of Ex-Situ Reduced Catalyst

	Oxygen Chemisorption, O/M	
Passivation Medium	**Nitrogen**	**Air**
H_2 Treatment Temperature Prior to Chemisorption		
- None	0.70	0.01
- 35°C	0.69	0.65
- 50°C	0.76	0.72
- 250°C	0.68	0.68

Example 3: Evaluation of Ex-situ Reduced and Dry Passivated Catalysts

[0019] The reduced and passivated catalyst samples from Example 2 were loaded into a pilot plant reactor and the performance of each catalyst was evaluated for hydrofinishing a hydrotreated 600N dewaxed oil. The dewaxed oil was previously hydrotreated to reduce the sulfur content to about 200 wppm.

[0020] Approximately 5 cc of three, ex-situ reduced and passivated noble metal catalysts were loaded into an upflow micro-reactor. These included noble metal catalysts that were all ex-situ reduced and passivated by (1) immersion in excess oil, as currently practiced, (2) exposure to ambient air or (3) pore filing with mineral oil. The catalysts were heated to 150°C in hydrogen with 2 psi water partial pressure, simulating a typical commercial start-up with recycled hydrogen and treat gas scrubbing. Oil feed was then started and operating conditions were adjusted to 2 LHSV, 1000 psig, and 2,500 scf/bbl. Reactor temperature was increased to 275°C and then held constant for about 7-10 days. Hydrogen purity was 100% and no gas recycle was used.

[0021] For comparison, a sample of commercial catalyst was reduced in-situ, and performance was then evaluated for hydrofinishing the same 600N dewaxed oil. In this case, the catalyst was loaded using the same procedure and then dried in nitrogen at 260°C, cooled to room temperature, reduced in dry hydrogen at about 260°C, and then cooled to 150°C. This sequence represents a "best case" for a perfect in-situ reduction of the noble metal catalyst. Then oil feed was introduced and operating conditions were adjusted as described above.

[0022] Product quality as defined by aromatics, sulfur, and nitrogen contents was monitored daily. Aromatics were measured by UV absorption (mmoles/kg). Total aromatics as a function of time on stream are shown in Figure 1. As shown, the initial aromatic saturation (arosat) performance of all ex-situ hydrogen reduced and passivated catalysts are equivalent to, or better than, the in-situ reduced catalyst. Further, the samples that were ex-situ reduced and dry passivated, either with air or by filling the pores with oil, had better aromatic saturates performance than the ex-situ reduced sample that was passivated by immersion in white oil.

Advantage of Dry Oil Over Air Passivated

[0023] The example below compares the performance of the two dry passivated catalysts of Example 2, air and oil pore-filled to protect the reduced noble metals, under more severe start-up conditions. In addition to passivation of the reduced metals, the oil pore-filled technique also offers the advantage of minimizing water adsorption by the catalyst during storage and handling, and therefore reducing water evolution during start-up and further mitigating the risk for metal sintering.

[0024] Hydrotreated dewaxed oil was used as the process feedstcock for catalyst evaluation. This oil is a dewaxed oil (-18°C) containing traces level of sulfur (4.7 wppm) and approximately 5.5 wt% aromatics (124 mmol/kg).

Example 4: Oxide Catalyst

[0025] The wet-gases treatment on the oxide catalyst was a base case against which air and oil passivated catalyst performance was compared. The noble metal catalyst in its oxide state was subjected to a drying step (140°C) and a reduction step (220°C) with wet gases containing about 2.2 psia water partial pressure. Previous studies have shown that under these reduction conditions metal sintering will occur resulting in a lower performing catalyst.

[0026] Towards the end of the wet gases treatment, and as the unit conditions were changed, the catalyst was subjected to an increase in water partial pressure to 3.5 psia for about 1 hour, at 150°C, prior to switching to dry hydrogen. The unit pressure was then slowly increased to 2000 psig operating pressure, and the dewaxed oil was introduced. Subsequently, reactor temperature was increased to the operating temperature of 220°C.

[0027] In addition, catalyst performance was again compared to the performance of the oxide catalyst that was dried and reduced using the conventional pilot plant start-up with dry-gases. This catalyst was dried in N_2 at 150°C and reduced in H_2 at 250°C for 8 hours.

[0028] As expected, treatment of the oxide catalyst with wet gases resulted in a lower performing catalyst than that for the dry treatment. The oxide wet and dry gases treated catalyst performances are summarized in Table 3 and Figure 2.

TABLE 3

		Total Aromatics, mmol/kg		% Hydrogenation	
MB #	Hrs on Oil	F-1 Oxide Wet N2 - Wet H2	F-2 Oxide Dry N2 - Dry H2	F-1 Oxide Wet N2 - Wet H2	F-2 Oxide Dry N2 - Dry H2
1	56	1.705	1.756	98.63	98.58
2	78	N/a	2.193	N/a	98.23
3	101	5.262	2.892	95.76	97.67
4	124	5.973	3.201	95.18	97.42
5	148	6.911	3.394	94.43	97.26
6	172	9.133	3.567	92.64	97.12
7	196	10.631	3.803	91.43	96.93

Example 5: Air and Oil Pore-Filled Passivated Catalysts

[0029] The air and oil pore-filled reduced and passivated catalysts were all subjected to wet-gas treatment. Two reactors were loaded with the air-passivated catalyst. One catalyst was subjected to a 2 hours drying step (140°C) and a 16 hours reduction step (140°C) with wet gases containing about 1-psia water partial pressure. The second air-passivated catalyst was directly reduced with wet hydrogen at 140°C for 16 hours, eliminating the drying step.

[0030] Two other reactors were loaded with the oil pore-filled passivated catalyst in, either extrudates or crush form. The two reactors were maintained under a static dry nitrogen pressure (200 psig) while the other catalysts were treated. Wet hydrogen (1-psia) was processed over the oil pore-filled passivated catalyst for about 4 hours at 140°C before switching to dry hydrogen gas.

Results

[0031] Figure 3 and Table 4 indicate lower performance of the air

[0032] Figure 3 and Table 4, indicate lower performance of the air passivated catalysts when treated with wet nitrogen and hydrogen. It is clear that the catalyst activity is significantly lower to that of the catalyst dried and reduced with dry gases.

[0033] The hydrogenation performance of the air-passivated catalyst subjected to wet hydrogen only was found to be marginally higher than that of the oxide catalyst of Example 4 treated with wet nitrogen and wet hydrogen.

TABLE 4

		F-1 Red./Air Pass. Wet N_2 - Wet H_2 *Crushed*		F-2 Red./Air Pass. No N_2 - Wet H_2 *Crushed*		F-3 Red./OilPass. No N_2 - Wet H_2 (short) *Crushed*		F-4 Red./Air Pass. No N_2 - Wet H_2 (short) *Extrudate*	
WB #	Hrs on Oil	T. Aromatics (mmol/kg)	% Hydrogenation	T. Aromatics (mmol/kg)	% Hydrogenation	T. Aromatics (mmol/kg)	% Hydrogenation	T. Aromatics (mmol/kg)	% Hydrogenation
1	104.4	3.611	97.09	3.526	97.16	n/a	n/a	1.756	98.58
2	128.4	5.176	95.83	4.940	96.02	2.941	97.63	2.193	98.23
3	151.3	6.458	94.79	5.431	95.62	1.512	98.78	2.892	97.67
4	174.2	6.861	94.47	5.934	95.21	1.734	98.60	3.201	97.42
5	196.5	7.042	94.32	6.314	94.91	1.804	98.55	3.394	97.26
6	219.4	7.275	94.13	6.437	94.81	1.910	98.46	3.567	97.12
7	242.3	7.488	93.96	6.352	94.88	2.070	98.33	3.803	96.93
Increased Temp. to 300°C under H_2 flow (no oil flow) - 12 hrs at 300°C and back to 220°C. Feed in at 220°C									
8	260.1	4.799	96.13	3.906	96.85	1.287	98.96	2.553	97.94
9	289.6	5.886	95.25	5.467	95.59	2.180	98.24	3.955	96.81
10	308.7	6.04	95.13	5.477	95.58	2.392	98.07	4.440	96.42

[0034] Figure 4 and Table 4, show that oil pore-filled passivated catalyst performance is similar to that of the oxide catalyst of Example 4 dried and reduced following the conventional pilot plant procedure, using dry gases. These results would indicate that no significant metal sintering occurred and that the active metal was fully accessible for the hydrogenation reaction.

[0035] The small performance differences observed between the extrudates and the crush catalysts could be a result of a better packing when using crushed catalyst in the small diameter reactor or perhaps mass transfer restrictions.

CLAIMS

1. A process for ex-situ reduction and dry passivation of a supported noble metal oxide catalyst having pores comprising

(a) reducing said catalyst in the presence of hydrogen and inert gas, to produce a reduced catalyst,

(b) passivating the reduced catalyst so that the catalyst remains dry and free flowing by a process including cooling in an inert atmosphere and filling the pores of the catalyst with oil, in the absence of excess liquid.

2. The process of claim 1, wherein said inert atmosphere is nitrogen.

3. The process of claim 1, wherein said oil is white oil.

4. The process of claim 1, wherein said oil is paraffinic oil.

5. The process of claim 1, wherein said oil is a low sulfur distillate.

6. The process of claim 1, wherein said catalyst is palladium and platinum supported on MCM-41.

7. The process of claim 1, wherein said noble metal is palladium and platinum.

8. The process of claim 1, wherein said support is a mesoporous or zeolitic matrix.

9. A process for ex-situ reduction and dry passivation of a supported noble metal oxide catalyst having pores comprising

(a) reducing said catalyst in the presence of hydrogen and inert gas, to produce a reduced catalyst,

(b) passivating the reduced catalyst so that the catalyst remains dry and free flowing by a process including cooling in an inert atmosphere and exposing the catalyst to air.

10. The process of claim 9, wherein said noble metal is palladium and platinum.

11. The process of claim 9, wherein said support is a mesoporous or zeolitic matrix.

12. The process of claim 9, wherein said catalyst is palladium and platinum supported on MCM-41.