In order to design a thermally durable NO\textsubscript{x} trap, there is a need to understand the changes in the microstructure of materials that occur during various modes of operation (lean, rich, and lean-rich cycles). This information can form the basis for selection and design of new NO\textsubscript{x} trap materials that can resist deterioration under normal operation.

**Microstructural Changes in Production Lean NO\textsubscript{x} Traps on Aging**

- **Pulsator Aging**
  - Lean and rich aged samples showed that the sintering of platinum particles occurs during aging and that barium migrates into the ceria-zirconia layer.
  - Both of these factors reduce platinum-barium oxide surface area where NO\textsubscript{x} can be adsorbed.
  - Sintering is less severe for lean-aged samples than for rich-aged samples.

- **Dyno Aging**
  - The analysis of on-vehicle evaluated samples after 32,000 km and 50,000 km showed that the bulk of precious metal sintering occurred in the early stages of on-vehicle aging.

**Model Catalysts**

- **Catalyst A**: 2\%Pt, 10\%CeO\textsubscript{2}-ZrO\textsubscript{2}-90\%BaO•6Al\textsubscript{2}O\textsubscript{3}
  - Impregnate alumina with barium salts and thermally treat in air to obtain BaO•6Al\textsubscript{2}O\textsubscript{3}.
  - Impregnate BaO•6Al\textsubscript{2}O\textsubscript{3} with lanthanum salts and thermally treat in air to obtain Lanthanum alumina.
  - Ball mill 2\%La\textsubscript{2}O\textsubscript{3}-98\%BaO•6Al\textsubscript{2}O\textsubscript{3} with commercial CeO\textsubscript{2}-ZrO\textsubscript{2} and Pt salts and thermally treat to obtain model NO\textsubscript{x} trap.

- **Catalyst B**: Pt/Al\textsubscript{2}O\textsubscript{3}
  - Impregnate alumina with Pt salts and thermally treat to obtain model NO\textsubscript{x} trap.

- **Catalyst C**: 2\%Pt, 5\%MnO\textsubscript{2}-93\%CeO\textsubscript{2}-ZrO\textsubscript{2}-90\%BaO•6Al\textsubscript{2}O\textsubscript{3}
  - Impregnate 2\%Pt-98\%CeO\textsubscript{2}-ZrO\textsubscript{2} with manganese salts and thermally treat to obtain model NO\textsubscript{x} trap.

**Aging Studies on Ex Situ Reactor**

**Lean-Rich Cycle Aging (500°C, 4 h) of Model Catalyst A [240 s - 60 s cycle]**

- **Fresh Sample**
  - Pt particle size in 0.5 - 2.5 nm range.
  - Change in location.

- **After 4 hours**
  - Pt particle size in 0.5 - 4.3 nm range.
  - Change in location.

- **After 8 hours**
  - Pt particle size in 0.5 - 4.5 nm range.
  - No change in location.

- **After 16 hours**
  - No further change compared to 12 hour samples.

**Combining Theory and Experiments**

Is it possible to examine computationally complex but experimentally simple systems by both theoretical and experimental methods?

**Forecast Improvements**

- **Optimize Performance**
  - Pt, Pd, Rh and/or Ni/Al\textsubscript{2}O\textsubscript{3} with support.

**Density Functional Theory Calculations**

- Generalized gradient approximation (PW91 functional).
- Spin polarization to capture correct ground state.
- Oxidation energy of PtxOy clusters calculated as:
  \[ E = E_{\text{ox}} - E_{\text{red}} = (\text{Pt-O}) E_{\text{Pt}} + E_{\text{O}} \]

- Convergence of results verified.

**Theoretical Model tells us that…**

- Pure Pt clusters are easily oxidized; supported Pt nanoparticles should primarily be in oxidized forms in an oxidizing environment.
- +4 oxidation state (i.e., Pt:O=1:2) is favored thermodynamically for Pt atoms.
- Pt clusters on a variety of oxidized supports differ in oxidation state.
- Support properties of O\textsubscript{2}, O\textsubscript{2-} and CO on Pt clusters are very different compared to an extended Pt surface.
- Experimental results suggest that Pt oxide clusters are structurally complex, although patterns can be detected and may aid in future analysis.

**Experimental Model Catalyst…**

- Pt clusters on a variety of oxidized supports differ in oxidation state.
- Theoretical calculations suggest that the Pt atom should be oxidized.

**Publications**


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