Destruction of mixed radioactive wastes of nuclear energy industry

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In this lecture the following new developments and applications of catalysis for environmental protection will be presented

1. Destruction of mixed radioactive wastes of nuclear energy industry.

2. Oxidation of unsymmetrical dimethylhydrazine over oxide and noble metal catalysts. Solution of environmental problems of production, storage and disposal of highly toxic rocket fuel.

3. Monolithic supported Mn-containing catalysts for ammonia decomposition and hydrogen sulfide adsorption from coal gas.

4. Optimum parameters of synthesis of Cu-ZSM-5 catalyst for reduction of $\text{NO}_X$ with hydrocarbons.

5. Ozone-catalytic oxidation of volatile organic compounds.
1. Destruction of mixed radioactive wastes of nuclear energy industry
Nuclear Energy and Environment

Nuclear Energy Production:
No direct emissions of NO\textsubscript{x}, CO, HC

Thermal Power Production:
SO\textsubscript{x} - 13 kg/Gcal; \hspace{1cm} NO\textsubscript{x} - 2 kg/Gcal

Is Nuclear Power Environmentally Safe

Yes \hspace{2cm} ??? \hspace{2cm} No

No direct environment pollution \hspace{2cm} The formation of substantial amount of mixed radioactive wastes
MAIN SOURCES OF WASTE IN NUCLEAR INDUSTRY

• uranium ore mining and processing
• production of fuel for power stations
• reprocessing of spent fuel
• weapons production and dismantling
• equipment decontamination
• remediation of nuclear sites
MIXED WASTE

Mixed waste is waste that contains both hazardous organic compounds and radioactive components.

Sources: uranium mill tailings, production of fuel and assembling of fuel rods for reactors, reprocessing of spent fuels from defense or commercial reactors; hospital & industrial “trash”

Composition:
Radionuclides: Cs-134,137; Sr-90; Am-241; Pu-238,239; U-235,238; I-131.
Heavy Metals: Pb, Cr, Hg
Organics:
- Lubricants, vacuum pump oils
- Solvents, toluene, chlorinated hydrocarbons
- PCB’s, PAH
- Extractants, tributyl phosphate
# Environmental Catalysis in Radioactive Waste Processing

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Method of processing or storage</th>
<th>Problem</th>
<th>Application of catalysis</th>
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<tbody>
<tr>
<td>Mixed organic waste</td>
<td>Incineration in flame</td>
<td>Air pollutants, radioactive aerosols</td>
<td>Alternative: catalytic combustion</td>
</tr>
<tr>
<td>Mixed organic waste</td>
<td>Molten salt oxidation</td>
<td>High temp., corrosion and NO\textsubscript{x} formation</td>
<td>Application of catalytically active melts</td>
</tr>
<tr>
<td>Mixed waste</td>
<td>Plasma arc destruction</td>
<td>High NO\textsubscript{x} concentration up to 10000 ppm</td>
<td>SCR of NO\textsubscript{x}</td>
</tr>
<tr>
<td>HLW containing nitrates</td>
<td>Vitrification</td>
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<td>Vitrification</td>
<td>High NO(_x) concentration up to 10000 ppm</td>
<td>Reduction of nitrates to N(_2) + NH(_3), followed by catalytic NH(_3) oxidation to N(_2)</td>
</tr>
<tr>
<td>Liquid HLW</td>
<td>Storage in tanks</td>
<td>H(_2) formation at explosive concentration</td>
<td>Catalytic oxidation of H(_2)</td>
</tr>
<tr>
<td>Contaminated soil and water</td>
<td>Remediation of nuclear sites</td>
<td>Formation of VOCs</td>
<td>VOC catalytic (photocatalytic) oxidation</td>
</tr>
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PROBLEMS OF MIXED WASTE DESTRUCTION

- Mixed waste has a number of dangerous properties:
  - flammability
  - explosiveness
  - toxicity
  - radioactivity

- Main requirements to technology:
  - minimization of radioactive and toxic emissions
  - minimization of secondary waste streams
  - minimization of danger of fire and explosions

Flame incineration of mixed wastes does not meet these requirements

- atmospheric pollutants: NOx, CO, HC, dioxins, etc.
- radioactive aerosol particles
- secondary radioactive waste streams
**BIC process of catalytic fluidized bed combustion**

- use of catalysts for complete oxidation
- use of the fluidized catalyst bed
- stoichiometric air/fuel ratio close to 1
- simultaneous heat evolution and consumption in the same catalyst bed
Principles of Technology of Mixed Organic Wastes
Catalytic Destruction

- complete destruction of hazardous organic components without secondary emissions
- compaction, more than 10000 fold reduction of volume of radioactive waste for further processing by existing technologies, vitrification
ADVANTAGES OF MIXED WASTE DESTRUCTION IN CATALYTIC FLUIDIZED BED

• low operation temperature (600-750°C)
• sharp decrease in toxic emissions of NO_x, CO, carcinogenic hydrocarbons
• low-temperature form of PuO_2 is easy to process by aqueous recovery method
• exclusion of the use of special refractory materials
• possibility to treat wastes with low calorific value without additional fuel.
# CHARACTERISTICS OF CATALYSTS

**Composition:**  
20% MgCr$_2$O$_4$/γ-Al$_2$O$_3$  
20% Cu$_x$Mg$_{(1-x)}$Cr$_2$O$_4$/γ-Al$_2$O$_3$  
5% Fe$_2$O$_3$/γ-Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of granules, mm</td>
<td>1-2</td>
</tr>
<tr>
<td>BET area, m$^2$/g</td>
<td>120-180</td>
</tr>
<tr>
<td>Bulk density, g/cm$^3$</td>
<td>1.0-1.1</td>
</tr>
<tr>
<td>Crushing strength, MPa</td>
<td>40-50</td>
</tr>
<tr>
<td>Activity in C$<em>4$H$</em>{10}$ oxidation</td>
<td>$*10^2$ cm$^3$/g s (400°C)</td>
</tr>
</tbody>
</table>
Pilot installation

Goal - study of processes of catalytic fluidized bed destruction and off gas treatment with simulated wastes

1 - fluidized bed catalytic reactor; 2 - heat exchanger, 3-cyclone, 4 - CO catalytic converter, 5 - jet scrubber, 6 - absorber-condenser, 7 - aerosol filter
PILOT INSTALLATION
AT THE PLANT OF CHEMICAL CONCENTRATES (NOVOSIBIRSK)
Results of Pilot Plant Tests

Analysis of the exhaust gas after catalytic reactor

Catalyst 20%\(\text{MgCr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3\)

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Temperature in the FB reactor, °C</th>
<th>CO, ppm</th>
<th>NO, ppm</th>
<th>NO(_2), ppm</th>
<th>SO(_2), ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial oil</td>
<td>775</td>
<td>122</td>
<td>16</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>148</td>
<td>15</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Vacuum pump oil</td>
<td>745</td>
<td>116</td>
<td>9</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>110</td>
<td>10</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Compressor oil</td>
<td>770</td>
<td>122</td>
<td>19</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>85</td>
<td>18</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>
MONOLITHIC CATALYST FOR CO OXIDATION

Composition: 0.3%Pt/Al₂O₃, SiO₂, MgSiO₃

Dimensions, mm  72x72x75
Channel size, mm  2.2
Wall thickness, mm  0.45
BET area, m²/g  15
Pressure drop
at 6000 h⁻¹, Pa  40
CO conv. (1 vol. %)
at 10000 h⁻¹, 250°C  94
Results of monolithic catalyst testing for CO oxidation in flue gases of FB combustion of wastes

<table>
<thead>
<tr>
<th>$T,^\circ\text{C}$ in FB reactor</th>
<th>$T,^\circ\text{C}$ in CO converter</th>
<th>Initial CO conc. ppm</th>
<th>CO after the catalyst ppm</th>
<th>$X_{\text{CO}}$, %</th>
</tr>
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<tbody>
<tr>
<td>620</td>
<td>200</td>
<td>1976</td>
<td>134</td>
<td>93,2</td>
</tr>
<tr>
<td>750</td>
<td>230</td>
<td>135</td>
<td>0*</td>
<td>&gt; 99,4</td>
</tr>
<tr>
<td>740</td>
<td>235</td>
<td>320</td>
<td>6</td>
<td>98,0</td>
</tr>
<tr>
<td>765</td>
<td>240</td>
<td>104</td>
<td>0</td>
<td>&gt; 99,2</td>
</tr>
<tr>
<td>780</td>
<td>255</td>
<td>48</td>
<td>0</td>
<td>&gt; 98,3</td>
</tr>
</tbody>
</table>

*) accuracy of CO analyzer is 1 ppm
Study of Thorium Accumulation in Pilot Plant Units

Th captured, mg

Time, h

- Catalyst granules
- Catalyst particulates in cyclone
- Gas cleaning units
Distribution of Th over catalyst granule

X-Ray Microprobe Analysis
Prototype Demonstration Plant at the Plant of Chemical Concentrates (Novosibirsk)
CATALYTIC REACTOR OF PROTOTYPE DEMONSTRATION PLANT
Special Design of Nuclear Safe Annular FB Reactor

Nuclear Safety ⇔ Criticality ⇔ Critical maximum size of vessels, reactors, etc.

FB destruction proceeds in the annulus between two cylindrical walls