Studies of Size Selected Model Catalysts: Hydrazine decomposition over size selected Ir\(_n\)/Al\(_2\)O\(_3\) model catalysts

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Support: AFOSR
Background

• Overview of Experiment:
  
  – What do we do?
    
    • Attempt to further understand the chemistry taking place on catalytic surfaces.
    
    • We try to develop an understanding of the dependence of catalysis on cluster size.
  
  – How do we do it?
    
    • Beamline: Catalytic surfaces of interest are created by depositing various size selected metal nano-clusters onto various substrate materials.
    
    • UHV Chamber (Base Pressure ~ 3x10^{-10} torr): Prepared surfaces are analyzed and tested using an assortment of surface sensitive techniques.
Hydrazine/Ir/alumina

Why Hydrazine?
- Spacecraft thrusters, gas generators, power generation
- H₂ storage (CO free for fuel cells)

Problems:
- Sintering, support degradation
- High T stability (high Tₘₑₙₜ)
- Cold starts
- Low T chemistry (low Eₐ)

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<th>Eₐ (kJ)</th>
<th>m.p.(K)</th>
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Characterize low temperature chemistry v.s. Irₙ size
Characterize sintering behavior
Develop strategies for improvements
Metal clusters form within the source box in the presence of Helium after being vaporized by incoming laser radiation. Cation clusters are selectively guided through the beamline by a series of quadrupole ion guides and lenses. Cluster sizes of interest are selectively allowed to pass through the mass selector and be deposited on the substrate of interest within the UHV chamber.
Preparation of $\text{Al}_2\text{O}_3$/NiAl(110)

Freund recipe:
1. Ar$^+$ Sputter NiAl (110)
2. Anneal: 1000K, 20 min
   1220K, 10 min
3. $\text{O}_2$ 120L at 550K
4. Anneal: 950K, 10 min

O-terminated, 5 Å thick

Kulawik et al., PRL (2003) 256101
No previous data on $\text{N}_3\text{H}_4$/Ir/alumina below room temperature.

The multilayer desorbs intact providing us with an internal standard for the hydrazine cracking pattern.

With increasing coverage, a third peak forms with more binding energy than the original multilayer. This could signal the onset of a phase transition within the hydrazine multilayer.
Hydrazine TPD from High Coverage Model Catalyst

High coverage catalyst similar to bulk metal

0.5 ML Ir/alumina, annealed to 600K
2.7 L hydrazine dose at 95 K

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- 2.7 L hydrazine dose at 95 K

1. **Low T**
   - \( \text{N}_2\text{H}_4_{\text{ads}} \rightarrow \text{N}_2 \uparrow + 4\text{H}_{\text{ads}} \)
   - \( 2\text{H}_{\text{ads}} + \text{N}_2\text{H}_4_{\text{ads}} \rightarrow 2\text{NH}_3 \uparrow \)
   - \( 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \uparrow \)
   - \( \text{N}_2\text{H}_4_{\text{ads}} \rightarrow 2\text{NH}_2 \)

2. **Higher T**
   - \( \text{NH}_2_{\text{ads}} \rightarrow \text{NH}_{\text{ads}} + \text{H}_{\text{ads}} \)
   - \( \text{NH}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{H}_{\text{ads}} \)
   - \( \text{H}_{\text{ads}} + \text{NH}_2_{\text{ads}} \rightarrow \text{NH}_3 \uparrow \)
   - \( 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \uparrow \)
   - \( 2\text{N}_{\text{ads}} \rightarrow \text{N}_2 \uparrow \)
Hydrazine Pulse Dosing

Hydrazine pulsed onto catalyst while potential products leaving the surface are monitored with a mass spectrometer.

Temperature dependence of N₂, NH₃ and H₂

NH₄ pulsing on 0.5 ML Ir/Al₂O₃/NiAl(110) at 600 K

~1 sec pulse, broadened by desorption
N 1s XPS

N(1s) XPS on Al₂O₃ and 0.5 ML Ir/Al₂O₃

Also seen after TPD for 0.5 ML Ir/alumina

398 eV B.E. cyanide or nitride

No C signal \(\Rightarrow\) Nitride

No change in Ni or Ir XPS
Nitride Formation

$\text{Al}_x\text{O}_y\text{N}_z$ compound

No change in O 1s signal
No change in O ISS

No N ISS signal after TPD

-Sub-surface nitride
TPD of $\text{N}_2\text{H}_4$ on 0.1 ML Ir$_7$/Al$_2$O$_3$

Background:
Ionizer cracking
$\text{N}_2\text{H}_4 \rightarrow \text{N}_2^+, \text{NH}_3^+, \text{and H}_2^+$
Reaction at defects

Intensity (a. u.)

Temperature (K)
Correcting for N$_2$H$_4$ cracking

N$_2$ production in range from 155 K to $\sim$350 K

215 K for high coverage

No NH$_3$ from Ir$_7$/alumina

NH$_3$ similar to N$_2$ for high coverage

H$_2$ production $\sim$275 – 550 K

H$_2$ background high in UHV – switch to N$_2$D$_4$
ND$_3$ Production from Ir$_n$/Al$_2$O$_3$/NiAl
High coverage v.s. Small Clusters

0.5 ML Ir/alumina, annealed to make clusters

Low T
\[ \text{N}_2\text{H}_4 \text{ads} \rightarrow \text{N}_2 + 4\text{H}_{\text{ads}} \]
\[ 2\text{H}_{\text{ads}} + \text{N}_2\text{H}_4 \text{ads} \rightarrow 2\text{NH}_3 \uparrow \]
\[ 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \uparrow \]
\[ \text{N}_2\text{H}_4 \text{ads} \rightarrow 2\text{NH}_2 \]

Higher T
\[ \text{NH}_2 \text{ads} \rightarrow \text{NH}_{\text{ads}} + \text{H}_{\text{ads}} \]
\[ \text{NH}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{H}_{\text{ads}} \]
\[ \text{H}_{\text{ads}} + \text{NH}_2 \text{ads} \rightarrow \text{NH}_3 \uparrow \]
\[ 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \uparrow \]
\[ 2\text{N}_{\text{ads}} \rightarrow \text{N}_2 \uparrow \]
\[ \text{N}_{\text{ads}} \rightarrow \text{Nitride Formation} \]

Size Selected Ir$_n$/alumina

Low T
\[ \text{N}_2\text{H}_4 \text{ads} \rightarrow \text{N}_2 + 4\text{H}_{\text{ads}} \]
\[ 2\text{H}_{\text{ads}} + \text{N}_2\text{H}_4 \text{ads} \rightarrow 2\text{NH}_3 \uparrow \]
\[ 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \uparrow \]
\[ \text{N}_2\text{H}_4 \text{ads} \rightarrow 2\text{NH}_2 \]

Higher T
\[ \text{NH}_2 \text{ads} \rightarrow \text{NH}_{\text{ads}} + \text{H}_{\text{ads}} \]
\[ \text{NH}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{H}_{\text{ads}} \]
\[ \text{H}_{\text{ads}} + \text{NH}_2 \text{ads} \rightarrow \text{NH}_3 \uparrow (\text{Ir}_{15}) \]
\[ 2\text{H}_{\text{ads}} \rightarrow \text{H}_2 \uparrow \]
\[ 2\text{N}_{\text{ads}} \rightarrow \text{N}_2 \uparrow \]

Little Nitride formation
N₂ TPD from Irₙ/alumina

Sub-surface layer desorption

Hydrazine cracking contribution subtracted

Intensity of N₂ (a. u.)

Temperature (K)
alumina/NiAl(110) structure

STM from Kulawik et al. PRL (2003) 256101


Gaps between Al$_2$O$_3$ film and NiAl substrate give rise to sub surface nitrides when dosing w/ N$_2$H$_4$
Passivated Alumina/NiAl(110)

Small N 1s signal 398 eV:
No N ISS or other changes
Sub-surface Nitride
Much less efficient w/o Ir
Repeated cycles

Repeat until TPD reaches steady state
Dose ~10 ML N₂D₄ at ~100K
TPD to 800 K (desorbs everything)
Deposit clusters
TPD of Irᵣ/passivated Alumina

Ir₁₅ deposited at 100K, flashed to 300K to clean before hydrazine exposure
High temperature peaks are present for $\text{N}_2$ in the passivated catalyst.

Peak intensity and temperature is size-dependent for both products.
High coverage v.s. Small Clusters

0.5 ML Ir/alumina, annealed to make clusters

Low T
\[ \text{N}_2\text{H}_4 \text{ads} \rightarrow \text{N}_2 \uparrow + 4\text{H}_\text{ads} \]
\[ 2\text{H}_\text{ads} + \text{N}_2\text{H}_4 \text{ads} \rightarrow 2\text{NH}_3 \uparrow \]
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Higher T
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\[ \text{NH}_\text{ads} \rightarrow \text{N}_\text{ads} + \text{H}_\text{ads} \]
\[ \text{H}_\text{ads} + \text{NH}_2 \text{ads} \rightarrow \text{NH}_3 \uparrow \]
\[ 2\text{H}_\text{ads} \rightarrow \text{H}_2 \uparrow \]
\[ 2\text{N}_\text{ads} \rightarrow \text{N}_2 \uparrow \]
\[ \text{N}_\text{ads} \rightarrow \text{Nitride Formation} \]

Size Selected Ir\textsubscript{n}/alumina PASSIVATED

Low T
\[ \text{N}_2\text{H}_4 \text{ads} \rightarrow \text{N}_2 \uparrow + 4\text{H}_\text{ads} \]
\[ 2\text{H}_\text{ads} + \text{N}_2\text{H}_4 \text{ads} \rightarrow 2\text{NH}_3 \uparrow \]
\[ 2\text{H}_\text{ads} \rightarrow \text{H}_2 \uparrow \]
\[ \text{N}_2\text{H}_4 \text{ads} \rightarrow 2\text{NH}_2 \]

Higher T
\[ \text{NH}_2 \text{ads} \rightarrow \text{NH}_\text{ads} + \text{H}_\text{ads} \]
\[ \text{NH}_\text{ads} \rightarrow \text{N}_\text{ads} + \text{H}_\text{ads} \]
\[ \text{H}_\text{ads} + \text{NH}_2 \text{ads} \rightarrow \text{NH}_3 \uparrow \]
\[ 2\text{H}_\text{ads} \rightarrow \text{H}_2 \uparrow \]
\[ 2\text{N}_\text{ads} \rightarrow \text{N}_2 \uparrow \]
\[ \text{Nitride already formed} \]
What’s Next

Hydrazine/Ir/Alumina

- Fine tune the passivation process
- Finish Ir$_n$ TPD - When does NH$_3$ production kick in (new quad)
- Pulse dosing with Ir$_n$
- NH$_3$ and H$_2$ TPD / decomposition for comparison
- IRAS of N$_2$H$_4$ and NH$_x$ v.s. cluster size
- ISS and XPS of as-deposited, reacted, and sintered clusters.