Positive effect of Ga-promoting on the catalytic dehydrogenation of propane over a Pt catalyst

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http://www.lct.UGent.be

NCCC, Noordwijkerhout, The Netherlands, 08/03/2017
Catalytic propane dehydrogenation

Million Metric Tons Propylene

Propylene demand

Production gap

Need of on-purpose production route such as catalytic dehydrogenation of propane

Production via steam cracking (low selectivity)

C\textsubscript{3}H\textsubscript{8} → C\textsubscript{3}H\textsubscript{6} + H\textsubscript{2}

600°C

Pt-based catalyst

✓ High activity

✗ C\textsubscript{3}H\textsubscript{6} selectivity (~80%)

✗ Fast catalyst deactivation

✓ Co-feeding of H\textsubscript{2}

✓ Alloying with promoting element (e.g. Ga)
Ga-alloying (experiments)

C₃H₈ dehydrogenation experiments on Pt(-Ga) catalyst

<table>
<thead>
<tr>
<th>Input conditions</th>
<th>Siddiqi (2010) and Sun (2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>873 K</td>
</tr>
<tr>
<td>Total pressure</td>
<td>1.013 bar</td>
</tr>
<tr>
<td>Partial pressures</td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.20 bar</td>
</tr>
<tr>
<td>H₂</td>
<td>0.25 bar</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>0.025 g</td>
</tr>
<tr>
<td>Molar flowrates</td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.029 mol/hr</td>
</tr>
<tr>
<td>H₂</td>
<td>0.037 mol/hr</td>
</tr>
<tr>
<td>He</td>
<td>0.081 mol/hr</td>
</tr>
<tr>
<td>Active sites</td>
<td>0.03 (Pt) – 0.0248 (Pt-Ga)</td>
</tr>
<tr>
<td>Pt dispersion</td>
<td>84% (Pt) - 71% (Pt-Ga)</td>
</tr>
<tr>
<td>Pt wt% in catalyst</td>
<td>0.7 wt%</td>
</tr>
</tbody>
</table>


Combination of geometric and electronic effects

GOAL

Explain the positive effect of Ga-promoting on selectivity and coke formation based on DFT kinetics

Experiments performed on Pt-Ga/Mg(Ga)AlO\textsubscript{x} catalyst

\texttimes\hspace{1em} Exact Pt-Ga phase composition not accessible

\begin{itemize}
  \item Pt\textsubscript{2}Ga\textsubscript{3}, PtGa, Pt\textsubscript{5}Ga\textsubscript{3}, Pt\textsubscript{2}Ga, Pt\textsubscript{3}Ga
\end{itemize}

\textcolor{green}{\textbf{Most probable candidate:}}
\begin{itemize}
  \item non-segregated Pt\textsubscript{3}Ga
\end{itemize}

Wang (2009)
Computational approach

Density Functional Theory (DFT) calculations with periodic slab approach
- optPBE vdW-DF functional (long range interactions) (Dion 2004 and Klimes 2010)
- $4 \times 2$ Pt(111) and Pt$_3$Ga(111) unit cells

1 propylene/8 surface atoms:
Half of experimental monolayer coverage
(Lee 2001, Tsai 1997)

- Plane waves, PAW, 400 eV cut-off, no spin polarization
- First order Methfessel-Paxton smearing, $\sigma=0.20$ eV
- $3 \times 5 \times 1$ k-point Monkhorst-Pack grid
- TS determination: NEB, followed by dimer calculation
- $S$, $H$: statistical thermodynamics based on harmonic oscillator approach
Microkinetics and reactor modelling

Reactor model

PFR reactor model:
\[
\frac{dF_i}{dW} = R_i
\]

Rate coefficients

Transition state theory
\[
k = \frac{k_B T}{h} \exp \left( \frac{\Delta^\ddagger S}{R} \right) \exp \left( - \frac{\Delta^\ddagger H}{RT} \right)
\]

Reaction products calculated in separate unit cells

Kinetic model

- Surface species: \( \frac{d\theta_i^*}{dt} = R_{i^*} = 0 \)
- Pseudo-Stationary State Approximation (PSSA)
- All reaction steps are reversible
- 38 reactions in total

Type of reaction | Example
---|---
Ad-/desorption | \( \text{C}_3\text{H}_8 \rightleftharpoons \text{C}_3\text{H}_8,\text{physi} \)
Dehydrogenation | \( \text{C}_3\text{H}_8,\text{physi} \rightleftharpoons \text{CH}_3\text{-CH-CH}_3 + \text{H} \)
C-C scission | \( \text{CH}_3\text{-CH-CH}_3 \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{-CH}_3 \)
Isomerization | \( \text{CH}_3\text{-CH-CH}_3 \rightleftharpoons \text{CH}_2\text{-CH}_2\text{-CH}_3 \)
Deep dehydrogenation | \( \text{CH}_2\text{-CH-CH}_3 \rightleftharpoons \text{CH}_2\text{-C-CH}_3 + \text{H} \)
Coke formation | \( \text{C} \rightarrow \text{coke formation} \)

Coke formation reaction
- Active sites could be completely blocked
- Rate coefficient fitted to experimental data

Peng (2012)
Extensive reaction network

$\text{CH}_3-\text{CH}_2-\text{CH}_3,(g)$ propane

$\text{CH}_3-\text{CH}_2-\text{CH}_3,\text{physisorbed}$

1. $\text{CH}_2-\text{CH}_2-\text{CH}_3 + \text{H} \xleftrightarrow{} \text{CH}_3-\text{CH}-\text{CH}_3 + \text{H}$
   - 1-propyl

2. $\text{CH}_3-\text{CH}-\text{CH}_3 + \text{H}$
   - 2-propyl

3. $\text{CH}_3 + \text{CH}_2\text{CH}_3$
   - methyl ethyl

4. $\text{CH}-\text{CH}_2-\text{CH}_3 + \text{H}$
   - 1-propylidene

5. $\text{CH}_2-\text{CH}-\text{CH}_3 + \text{H}$
   - propylene

6. $\text{CH}_3-\text{C}-\text{CH}_3 + \text{H}$
   - 2-propylidene

7. $\text{CH}_3 + \text{CH}_2\text{CH}_3$

8. $\text{CH}_2-\text{CH}-\text{CH}_3,(g)$ propylene

NCCC, Noordwijkerhout, 08/03/2017
At experimental conversion (11.5 %):

✓ Simulations predict the experimentally obtained $\text{C}_3\text{H}_6$ selectivity (~79 %)

Fit rate coefficient of graphitic coke formation reaction to obtain realistic coke yields:

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<th>Simulated</th>
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<td>Coke formed (5’ TOS)</td>
<td>32.0</td>
<td>31.2</td>
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</table>

✓ No influence on conversion/selectivity

Siddiqi (2010)
Simulations on Pt$_3$Ga(111): selectivity and coke formation

### Selectivity

![Graph showing selectivity vs. conversion](chart.png)

- **Pt$_3$Ga(111):** Full selectivity (~100%)
- **Pt(111):** Selectivity drops significantly with conversion

- **Simulation predicts positive effect on selectivity (~99%)**

### Coke formation

**Amount of coke formed after 5’ TOS (mol$_C$/mol$_{Pt}$):**

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<td>18.0</td>
<td>$\sim 10^{-5}$</td>
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- **Simulation predicts positive effect on coke formation**

- **Same $k$ as on pure Pt(111)**

**Origin of ‘positive Ga-alloying effect’?**
Reaction path analysis

\[ \text{CH}_3\text{-CH}_2\text{-CH}_3,\text{(g)} \rightarrow \text{propane} \]

\[ \text{CH}_3\text{-CH}_2\text{-CH}_3,\text{physisorbed} \]

\[ \text{CH}_2\text{-CH}_2\text{-CH}_3 + \text{H} \rightarrow \text{CH}_3\text{-CH-CH}_3 + \text{H} \]

1-propyl

2-propyl

4

5

7

8

\[ \text{CH}_2\text{-CH-CH}_3 + \text{H} \rightarrow \text{CH}_3\text{-C-CH}_3 + \text{H} \]

1-propylidene

2-propylidene

\[ \text{CH}_2\text{-CH-CH}_3,\text{(g)} \rightarrow \text{propylene} \]

\[ \text{CH}_3 + \text{CH}_2\text{CH}_3 \rightarrow \text{methyl} + \text{ethyl} \]

\( E_a = 180 \text{ kJ/mol} \)

\( E_a = 183 \text{ kJ/mol} \)
Reaction path analysis

1-propylidyne

C-CH2-CH3 + H

Pt3

1-propylene

CH-CH-CH3 + H

Pt2 Pt

2-propylene

CH2-C-CH3 + H

Pt Pt2 Pt

propylene

H + C-CH-CH3

Pt Pt3Pt

1-propenyl

Pt

propenyldiene

H + C-CH-CH3

Pt Pt3Pt

2-propenyl

Pt

c

Pt(111)
Pt3Ga(111)

d

coke formation

methyldiene

methyldyne

Pt2

CH3-C + CH

Pt3 Pt3

Ea = 111 kJ/mol
Ea = 211 kJ/mol

ethyldiene

methylidyne

Pt

methyl

Pt

methane

CH4,(g)

ethane

CH3CH3,(g)

ethylene

C2H4-Pt

12
High barrier for C-C scission of propyne on Pt$_3$Ga(111)

→ no formation of ethylidyne and methylidyne

→ negligible formation of side products coke, CH$_4$, C$_2$H$_6$ and C$_2$H$_4$

→ geometric effect: smaller Pt ensembles
Increased selectivity on Pt$_3$Ga(111) due to geometric and electronic effects.

C$_3$H$_6$ adsorbs more strongly on Pt(111)

$\rightarrow$ electronic effect: C$_3$H$_6$ desorbs more easily from Pt$_3$Ga(111)
Origin very low coke formation

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→ Same $k$ as on pure Pt(111)

Simulated coke formation on Pt$_3$Ga(111) almost non-existent

→ assumption: graphitic coke originates from atomic C

atomic C is more stable on Pt(111)

Pt$_3$Ga(111): C is less stable than C$_3$H$_6$,ads
Coke formation on step sites?

- Pt(211) surface → include step sites

- Energetics at relevant reaction step for coke formation:

\[
\text{Pt}_2 \text{Pt}_2 \quad \xrightarrow{30} \quad \text{ethylidyne} \text{ methyldyne}
\]

\[
\text{Pt}(111): \Delta E_{\text{elec}} = -64 \text{ kJ/mol}, \ E_{a,\text{elec}} = 113 \text{ kJ/mol}
\]

\[
\text{Pt}(211): \Delta E_{\text{elec}} = -53 \text{ kJ/mol}, \ E_{a,\text{elec}} = 96 \text{ kJ/mol}
\]

- Selective blocking of defect sites by Ga atoms:

Ga prefers to sit in low-coordinated sites such as edges, kinks and steps:

Ga on surface step → Ga in (111) surface plane 22 kJ/mol

✗ Coke formation via atomic carbon or on step sites less likely for Pt$_3$Ga
Conclusions

Construct extensive reaction network using DFT calculations and perform reactor simulations.

Experiments: positive effect of Ga-alloying

Geometric and electronic effects explain the positive effect on $C_3H_6$ selectivity.

On $Pt_3Ga$ coke formation is less likely on step sites or via atomic carbon.

Selectivity $C_3H_6$ (%)
Acknowledgments

- The Long Term Structural Methusalem Funding by the Flemish Government.
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Back-up slides
Increasing Ga-content → shift of ~ -5 cm⁻¹

experimental (tabulated) gas-phase CO

2172(2176) → 2117(2120)

2085
2088
2090
2074
2071
2086
2089
2073
2073
2070
2088
2073
2085
2070

2083
2067

5Pt-HT-5Ga
5Pt-HT-1Ga
5Pt-HT-0Ga
5Pt-HT-5Ga
5Pt-HT-1Ga
5Pt-HT-0Ga

CO in the gas phase

no CO in the gas phase

Courtesy of E. Redekop
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Coverage $\theta_{\text{CO}}$</th>
<th>Shift from pure Pt (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>High coverage</td>
<td>-5</td>
</tr>
<tr>
<td>Pt$_3$Ga(111)</td>
<td>0.25</td>
<td>-19</td>
</tr>
<tr>
<td>Pt$_5$Ga$_3$(212)</td>
<td>0.25</td>
<td>-16</td>
</tr>
<tr>
<td>Pt$_2$Ga(011)</td>
<td>0.17</td>
<td>-39</td>
</tr>
<tr>
<td>Pt$_5$Ga$_3$(212)</td>
<td>0.13</td>
<td>-34 -22</td>
</tr>
<tr>
<td>PtGa(111)</td>
<td>0.17</td>
<td>-32</td>
</tr>
<tr>
<td>Pt$_2$Ga$_3$(110)</td>
<td>0.20</td>
<td>-41</td>
</tr>
</tbody>
</table>

- Best correspondence with experiment → anti-segregated Pt$_3$Ga
- However, non-segregated is more stable
- Non-segregated Pt$_3$Ga → most probable candidate
- Coverage dependence → even at same coverage for the other alloy models ($\theta_{\text{CO}} = 0.25$) → still non-segregated Pt$_3$Ga preferred
- Alloy with lowest amount of Ga → surface alloys (Pt$_3$Ga/Pt) show promising results (shift of 11 cm$^{-1}$)
Fit rate coefficient of graphitic coke formation reaction to obtain realistic coke yields:

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<td>molC/molPt</td>
<td></td>
<td></td>
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✓ No influence on conversion/selectivity
Experiment

Higher selectivity for Pt-Ga catalyst
- Smaller Pt ensembles (geometric)
- \( \text{C}_3\text{H}_6 \) adsorption strength ↓ (electronic)

Simulations

✓ Simulation predicts positive effect on selectivity (~99 %)
Experiment

Less coke formation for Pt-Ga catalyst

- Smaller Pt ensembles (geometric)
- $\text{C}_3\text{H}_6$ adsorption strength ↓ (electronic)

Simulations

Amount of coke formed after 5’ TOS (mol$_C$/mol$_{Pt}$)

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✓ Simulation predict positive effect on coke formation

$\rightarrow$ Origin of ‘positive Ga-alloying effect’?

Same $k$ as on pure Pt(111)
Table 3-1. Comparison of propylene/propane adsorption strength for two different functionals and experiment.

<table>
<thead>
<tr>
<th>$\Delta E_{ads}$ (kJ/mol)</th>
<th>Experimental data (0.2 ML) [24]</th>
<th>OptPBE vdW-DF (0.13 ML)</th>
<th>BEEF vdW-DF (0.13 ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene chemisorption</td>
<td>-68</td>
<td>-134</td>
<td>-105</td>
</tr>
<tr>
<td>Propane physisorption</td>
<td>-</td>
<td>-43</td>
<td>-33</td>
</tr>
</tbody>
</table>