Catalytic hydrogenation of benzene on Pillared Layered Structures

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**Clays and Pillared Clays (PILCs)**

**Scale-up of PILCs preparation**

**Benzene hydrogenation on Ni-PILCs**
- Ni in Perovskite (La-Ni) forms
- Ni on Al-Montmorilonite PILCs
- Ni on Al-Saponite PILCs
- Ni on Si-Montmorillonite PILCs

**Intraparticle Effects in PILC extrudates**

**Conclusions**
TECHNOLOGICAL BENEFITS OF CLAY MATERIALS

- They are naturally available materials
- They have adjustable acido-basic properties
- They possess high cationic exchange capacity (CEC)
- They can be pillared and obtain stable 2-dimensional structure

TECHNOLOGICAL INTEREST OF PILLARED CLAYS (PILCs)

- They possess high surface area and permanent porosity
  ➔ attractive solids for adsorption and catalysis purposes
- Their porosity can be localized in the larger micropore region
  ➔ they form a bridge between the microporous zeolites and the inorganic meso- and macroporous solids (e.g. silica, alumina)
(a) SiO$_4$ tetrahedron,
(b) Tetrahedrons condensing to form the tetrahedral sheet,
(c) Top view of the tetrahedral sheet. The dashed circles represent the oxygen atoms that are located above the plane designated by the remaining atoms

(a) Al or Mg-O-OH octahedron,
(b) Octahedron top view,
(c) Octahedrons condensing to form the octahedral sheet,
(d) Top view of the octahedral sheet.

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CLAY MINERAL structure

Clay Mineral Structure  

• Sheet upon sheet = layer
• Layer upon layer = crystal
• Layering tetrahedral and octahedral sheets together results in different clays

CLASSIFICATION OF CLAYS

Depending on the charge of the octahedral cation
• Dioctahedral (Al$^{3+}$), e.g. Beidelite
• Triocataedral (Mg$^{2+}$, Fe$^{2+}$, Li$^{2+}$), e.g. Hectorite, Saponite

Depending on the way the tetrahedral (T) and octahedral (O) sheets are combound
Common ratios are:
• 1 tetrahedral : 1 octahedral (1:1 or TO structures), e.g. Kaoline
• 2 tetrahedral : 1 octahedral (2:1 or TOT structures), e.g. Montmorillonite
Substitution of octahedral and tetrahedral cations by other elements with similar ionic radii and valence state. (e.g. Si$^{4+}$ by Al$^{3+}$, Al$^{3+}$ by Mg$^{2+}$, Mg$^{2+}$ by Li$^+$)

**Results:**
- Clay sheets negatively charged
- Large space in interlayer where water and other molecules or ions can be adsorbed and collected

Presentation of the triple sheet group (2:1) of mineral clays that includes smectites, micas, vermiculites, pyrophyllite and talc. The position between the clay sheets of a K$^+$ adsorbed counterion is also represented.
- Cation Exchange Capacity (CEC), in meq/100g clay
- The ability of the interlayer space to swell in polar medium
- Uneven distribution of cations in the interlayer space
- The ability of small cations to migrate into the clay lattice

Hoffman Klemen effect, (HK-effect) i.e. heating causes irreversible migration of small cations to the vacant sites in the clay layers

Hydration-dehydration behavior of a clay and a pillared clay

**Prerequisites for the pillaring process to be successful**

- The clay should have a moderate cation exchange capacity (CEC) to obtain the best swelling
- Alkali or alkaline earth ions in the interlayer space should easily be exchanged
- The pillaring cation is positively charged
- The pillaring cation must be dissolvable in the polar solvent used to swell the clay

**Factors influencing the choice of pillaring species**

- The thermal stability of the pillar
- The desired interlayer free spacings
- The chemical nature of pillars and their catalytic properties
- Their sensitivity to differences in the hydrolysis conditions
PILLARING SPECIES

- Organic cations e.g. N(CH_3)_4^+
- Organometallic cations e.g. (H_2N-Pr)_8Si_8^{8*}
- Oxide Sols e.g. TiO_2-SiO_2 sol
- Metal clusters e.g. Mo_8Cl_8^{4+}
- Polyoxycations e.g. Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}, [Al_{13}]
- Mixed Oxide Pillars e.g. LaNiO_3

Al_{13} Keggin ion

Si organometallic cation (H_2N-Pr)_8Si_8^{8*}

Perovskite of the form ABO_3
AZA
Pillared layers

Pillared aggregates within AZA

PILCs

Mesopores 20-500 Å

Micropores <20 Å

Macropores >500 Å

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Pillared Clays

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Scale-up Studies

Chemical analysis of AZA and FAZA (wt.% on dry basis)

<table>
<thead>
<tr>
<th></th>
<th>AZA</th>
<th>FAZA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52.66</td>
<td>52.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>27.55</td>
<td>27.56</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.85</td>
<td>7.02</td>
</tr>
<tr>
<td>CaO</td>
<td>0.84</td>
<td>0.35</td>
</tr>
<tr>
<td>MgO</td>
<td>2.19</td>
<td>2.50</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.32</td>
<td>1.38</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.20</td>
<td>0.27</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.60</td>
<td>0.17</td>
</tr>
<tr>
<td>LOI</td>
<td>12.5</td>
<td>7.50</td>
</tr>
</tbody>
</table>

220 ± 10 m²/g for AZA
**Intercalant preparation**

- Solution of 0.2 M AlCl₃ + NaOH 0.2 M
  - OH/Al = 1.9
  - \( t_{\text{addition}} = 1 \text{h} \)
  - \( t_{\text{ageing}} = 1 \text{h} \)
  - \( T = 70 \text{°C} \)

**Intercalation of clay**

- Pillaring solution + clay suspension
  - Al/dry clay = 3.8 mol/Kg
  - \( t_{\text{ageing}} = 18 \text{h} \)
  - \( T = 70 \text{°C} \)

**Washing & Filtering**

- Deiw + clay slurry
- Precipitation – decanting – redispersion
  - Conductivity of effluent < 30 \( \mu \text{s/cm} \)

**Drying**

- Lab scale: R.T.
  - (Room Temperature)
- Pilot scale: \( T = 60 \text{°C} \)
  - \( t_{\text{drying}} = 18 \text{h} \)

**Calcination**

- From \( 20 \text{°C} \)
- Stay at 495°C for 1h
- To 495°C: at 6h and 20min.

**Calcination**

- From 20°C
- Stay at 495°C for 1h

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# Main Properties of Pillared Clays (PILCs) Affecting Their Catalytic Activity

- Acidity (type and quantity)
- The ability of small cations to migrate into the clay lattice (HK-effect)
- Thermal stability up to 500°C.

<table>
<thead>
<tr>
<th>Type of clay</th>
<th>Pillar</th>
<th>Type of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>Tetramethylammonium</td>
<td>Oligomerization</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Triethylendiamine</td>
<td>Hydration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Esterification</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Al, Zr, (Al/Zr)</td>
<td>Catalytic cracking</td>
</tr>
<tr>
<td>Hectorite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Al, Zr</td>
<td>Disproportionation</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Al</td>
<td>Alkylation</td>
</tr>
<tr>
<td>Saponite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Al, Zr</td>
<td>Conversion of methanol</td>
</tr>
<tr>
<td>Bentonite</td>
<td>Al, Al/Zr</td>
<td>Oligomerization</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td></td>
<td>Isomerization</td>
</tr>
<tr>
<td>Bentonite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Empirical kinetic equation

\[ r = k \cdot P_B^m \cdot P_{H_2}^n \]

### Benzene Hydrogenation

\[ C_6H_6 + 3H_2 \rightarrow C_6H_{12} \]

<table>
<thead>
<tr>
<th>Type of catalyst</th>
<th>( m )</th>
<th>( n )</th>
<th>Conditions ( P, T )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-60 % Ni/SiO₂</td>
<td>0.5</td>
<td>-</td>
<td>( T=120^\circ C ) ( P_{H_2} = 680 ) Torr ( P_B = 50 ) Torr</td>
<td>Yoon και Vannice (1983)</td>
</tr>
<tr>
<td>11.3 % Ni/SiO₂</td>
<td>0.1</td>
<td>0.7</td>
<td>Same conditions ( P,T )</td>
<td></td>
</tr>
<tr>
<td>25 % Ni/Al₂O₃</td>
<td>0.3</td>
<td>1.3</td>
<td>Same conditions ( P,T )</td>
<td></td>
</tr>
<tr>
<td>10 % Ni/SiO₂</td>
<td>0.05</td>
<td>1.7</td>
<td>Same conditions ( P,T )</td>
<td></td>
</tr>
<tr>
<td>Ni/SiO₂, Al₂O₃, SiO₂·MgO</td>
<td>0</td>
<td>≈1</td>
<td>Same conditions ( P,T )</td>
<td></td>
</tr>
<tr>
<td>67% Ni/kieselguhr</td>
<td>0.2</td>
<td>0.3</td>
<td>Same conditions ( P,T )</td>
<td></td>
</tr>
<tr>
<td>Ni – SiO₂- Al₂O₃</td>
<td>0.24 - 0.41</td>
<td>0.3 - 0.35</td>
<td>( P = 760 ) Torr ( 130 &lt; T &lt; 200^\circ C )</td>
<td>Rusic και Zrncevic (1993)</td>
</tr>
<tr>
<td>Ni/SiO₂, Al₂O₃</td>
<td>0.26 - 0.30</td>
<td>1.15 - 1.50</td>
<td>( P = 760 ) Torr ( T &lt; 90^\circ C )</td>
<td>Marecot et al (1991)</td>
</tr>
<tr>
<td>Pt/SiO₂, n-Al₂O₃, SiO₂·Al₂O₃, TiO₂</td>
<td>0.1 ± 0.1</td>
<td>0.6 ± 0.1</td>
<td>44 &lt; T &lt; 83°C</td>
<td>Lin και Vannice (1993)</td>
</tr>
<tr>
<td>Ni/kieselguhr</td>
<td>0.6 - 0.8</td>
<td>0.5 - 0.7</td>
<td>119 &lt; T &lt; 195°C ( P_{H_2} = 919 ) Torr ( P_B = 1.2 ) Torr</td>
<td>Franco και Phillips (1980)</td>
</tr>
<tr>
<td>Pd/SiO₂, n-Al₂O₃, SiO₂·Al₂O₃, TiO₂</td>
<td>0 - 0.8</td>
<td>0.5 - 4</td>
<td>80 &lt; T &lt; 300°C ( P_{H_2} = 600 ) Torr ( P_B = 50 ) Torr</td>
<td>Chou και Vannice (1987)</td>
</tr>
</tbody>
</table>
V1: pressure regulator, V2: check valve, V3 - V11: on-off valves

ΔPM, PM: water and mercury pressure gauges for dP and P direct measurement. ST: sampling point

BENZENE HYDROGENATION

Differential Tubular Reactor Rig

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TYPICAL EXPERIMENTAL CONDITIONS

Reactor Loading
Catalyst mass: 0.1 – 0.3 gr / Inerts
Particle size: 0.160 – 0.315 mm

Catalyst Reduction
Reduction Temperature, $T_r$: 400 °C
Time at $T_r$: 2h
Heating rate: 1.5°C/min
Hydrogen flowrate: 1.5 Ncm³/s

Benzene Hydrogenation
Temperature range: 90 - 150°C
Deactivation check: 150°C
Inlet composition: $\frac{y_{\text{ben}}}{y_{\text{H}_2}} = 0.05$

ALTERATIONS

Reactor Loading
Catalyst mass: 0.04gr
Particle size: 0.630 – 0.800 mm, extrudates of various diameters

Benzene Hydrogenation
Deactivation check: 70°C

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Catalyst Preparation – Characterisation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%w/w La</th>
<th>%w/w Ni</th>
<th>SSA [m²/g cat]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A1) LaNiO₃-350-1</td>
<td>56.6</td>
<td>24.0</td>
<td>25</td>
</tr>
<tr>
<td>(A1) LaNiO₃-500-1</td>
<td>56.6</td>
<td>24.0</td>
<td>27</td>
</tr>
<tr>
<td>(A1) LaNiO₃-600-1</td>
<td>56.6</td>
<td>24.0</td>
<td>20</td>
</tr>
<tr>
<td>(A1) LaNiO₃-700-1</td>
<td>56.6</td>
<td>24.0</td>
<td>18</td>
</tr>
<tr>
<td>(A1) LaNiO₃-800-1</td>
<td>56.6</td>
<td>24.0</td>
<td>20</td>
</tr>
<tr>
<td>(A1) LaNiO₃-1000-1</td>
<td>56.6</td>
<td>24.0</td>
<td>8</td>
</tr>
<tr>
<td>(A2) LaNiO₃-500-2</td>
<td>56.6</td>
<td>24.0</td>
<td>27</td>
</tr>
<tr>
<td>(A2) LaNiO₃-600-2</td>
<td>56.6</td>
<td>24.0</td>
<td>17</td>
</tr>
<tr>
<td>(B1) 3LaNiO₃/AZA-500</td>
<td>4.4</td>
<td>1.8</td>
<td>174</td>
</tr>
<tr>
<td>(B1) 7LaNiO₃/AZA-500</td>
<td>10.2</td>
<td>4.3</td>
<td>155</td>
</tr>
<tr>
<td>(B1) 10LaNiO₃/AZA-500</td>
<td>14.6</td>
<td>6.1</td>
<td>142</td>
</tr>
<tr>
<td>(B1) 10LaNiO₃/AZA-600</td>
<td>15.3</td>
<td>6.4</td>
<td>99</td>
</tr>
<tr>
<td>(B2) 8LaNi/AZA-500</td>
<td>14.0</td>
<td>6.0</td>
<td>107</td>
</tr>
<tr>
<td>(C1) LaNiZA</td>
<td>14.0</td>
<td>6.0</td>
<td>112</td>
</tr>
</tbody>
</table>

- **Non-supported La-Ni systems (A)**
  1. Citrate method⁵ and self-ignition (LaNiO₃-x-1)
  2. Citrate method⁵ (LaNiO₃-x-2)

- **La, Ni system supported on AZA pillared clay catalysts (B)**
  1. Dry impregnations with the precursor solution of the LaNiO₃-x-y catalysts
  2. Dry impregnations with aqueous solutions of La (1) and Ni (2) nitrate salts (1 then 2) x 4

- **La, Ni system incorporated in the montmorillonite clay (C)**

---

Perovskite phase is formed after calcination.

The evolution of the perovskite crystallite structure depends on the calcination temperature as well as on the mode of preparation.

For all the supported La,Ni systems no perovskite phase was observed mainly due to:

- relatively low calcination temperature, 500 °C, of LaNiZA or AZA supported systems.
- the restricted area between the clay sheets prevented the LaNiOx oxides from forming the perovskite phase.


(a) X-ray diffractions of both the non-supported La-Ni series catalysts calcined at 500°C

(b) X-ray diffractions of both the non-supported La-Ni series catalysts calcined at 600°C

Dots correspond to the peaks consistent with the LaNiO₃ perovskite phase
CATALYST PREPARATION – CHARACTERISATION

- Dry impregnations of AZA with Ni nitrate salts (xNiAZA)

- AZA ion exchange with Al³⁺ and dry impregnations with Ni nitrate salts (Alie-xNiAZA)

- Zenith-N clay ion exchange with Al³⁺ and dry impregnations with Ni nitrate salts (Alie-xNiZ)

- AZA preparation under ratio OH/Al=0.5, ion exchange with Al³⁺ and dry impregnation with Ni nitrate salts (Alie-2NiA\textsubscript{0.5}ZA)

- AZA preparation with instant drying after pillaring of AZA precursor at 350°C and dry impregnations with Ni nitrate salts (4NiDAZA)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%w/w Ni</th>
<th>SSA [m²/g\textsubscript{cat}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zenith-N</td>
<td>-</td>
<td>44</td>
</tr>
<tr>
<td>AZA</td>
<td>-</td>
<td>225 ± 10</td>
</tr>
<tr>
<td>2NiAZA</td>
<td>2</td>
<td>198</td>
</tr>
<tr>
<td>4NiAZA</td>
<td>4</td>
<td>185</td>
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<tr>
<td>6NiAZA</td>
<td>6</td>
<td>190</td>
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<tr>
<td>8NiAZA</td>
<td>8</td>
<td>174</td>
</tr>
<tr>
<td>12NiAZA</td>
<td>12</td>
<td>162</td>
</tr>
<tr>
<td>18NiAZA</td>
<td>18</td>
<td>146</td>
</tr>
<tr>
<td>24NiAZA</td>
<td>24</td>
<td>134</td>
</tr>
<tr>
<td>Alie-2NiAZA</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>Alie-4NiAZA</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Alie-8NiAZA</td>
<td>8</td>
<td>174</td>
</tr>
<tr>
<td>Alie-12NiAZA</td>
<td>12</td>
<td>146</td>
</tr>
<tr>
<td>Alie-18NiAZA</td>
<td>18</td>
<td>129</td>
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<tr>
<td>Alie-4NiZ</td>
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<td>46</td>
</tr>
<tr>
<td>Alie-6NiZ</td>
<td>4</td>
<td>45</td>
</tr>
<tr>
<td>Alie-8NiZ</td>
<td>8</td>
<td>45</td>
</tr>
<tr>
<td>Alie-2NiA0.5ZA</td>
<td>2</td>
<td>51</td>
</tr>
<tr>
<td>4NiDAZA</td>
<td>4</td>
<td>89</td>
</tr>
</tbody>
</table>

UGent/FCh13/8-9L Ni-Al/PILCS Catalyst (Montmorillonite)

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XRD CATALYST CHARACTERISATION

- The well shaped peak for AZA PILC indicates d001-basal spacing of 18.2 Å. By subtracting the thickness of a montmorillonite layer (9.6 Å) we obtain the mean pillar height and the interlayer distance being 8.6 Å.

- The d001 distance of the parent clay Zenith-N is somewhat higher than the thickness of a single clay layer. This is due to hydrated interlayer cations.

- For the 24NiAZA catalyst, no peak consistent to Ni crystals is observed, verifying that all Ni particles formed upon agglomeration on the pillared clay surface are much smaller than 5nm.


XRD patterns of the supports and of the catalyst with the higher Ni loading.
CATALYST PREPARATION – CHARACTERISATION

- Dry impregnations of ATOS with Ni nitrate salts \((x\text{NiATOS})\)

- Dry impregnation of AZATOS (1:1 w/w mixture montmorillonite and saponite) with Ni nitrate salts \((4.4\text{NiAZATOS})\)

- Treatment of ATOS with polyphosphate aqueous solution (Calgon) and dry impregnation with Ni nitrate salts, \((4.2\text{NiM.E.-ATOS})\)

- Treatment of 4.2NiATOS with KOH 0.1N solution \((\text{Pas-4.2NiATOS})\)

- Treatment of ATOS with KOH 0.1N solution and dry impregnation with Ni nitrate salts \((4.2\text{Ni-PasATOS})\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%w/w Ni</th>
<th>SSA [m²/gcat.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATOS</td>
<td>-</td>
<td>230 ± 15</td>
</tr>
<tr>
<td>AZATOS</td>
<td>-</td>
<td>252</td>
</tr>
<tr>
<td>2.1NiATOS</td>
<td>2.1</td>
<td>194</td>
</tr>
<tr>
<td>4.2NiATOS</td>
<td>4.2</td>
<td>171</td>
</tr>
<tr>
<td>8.4NiATOS</td>
<td>8.4</td>
<td>181</td>
</tr>
<tr>
<td>12.6NiATOS</td>
<td>12.6</td>
<td>141</td>
</tr>
<tr>
<td>18.9NiATOS</td>
<td>18.9</td>
<td>102</td>
</tr>
<tr>
<td>4.4NiAZATOS</td>
<td>4.4</td>
<td>195</td>
</tr>
<tr>
<td>4.2NiM.E.-ATOS</td>
<td>4.2</td>
<td>141</td>
</tr>
<tr>
<td>Pas-4.2NiATOS</td>
<td>4.2</td>
<td>134</td>
</tr>
<tr>
<td>4.2Ni-PasATOS</td>
<td>4.2</td>
<td>155</td>
</tr>
</tbody>
</table>

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The support prepared out of a 1:1 mixture of pillared montmorillonite and saponite (AZATOS) presents a clear and sharp peak, representing a d001-basal spacing of 18.55 Å, thus a pillar height of approximately 9 Å. The microporosity formed seems better organized in AZATOS than in ATOS support, with uniform pillar height.

The X-ray pattern also implies a material out of well-stacked clay lamellas and a nearly constant pillar height.
| Clay slurry | 1 % w/w suspension of Zenith-N |
| Intercalant Preparation | Mixing of reagents in a ratio of \( \text{Ni(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}:\text{MeOH}:\text{APTEOS} = 1:2.3:4.57 \)  APTEOS : 3-aminopropyl-triethoxysilane |
| Intercalation of clay | APTEOS/Zenith-N ratio = 8 mol/Kg  
\( t_{\text{ageing}} = 30 \text{ min R.T.} \) (Room Temperature) |
| Hydrolysis | \( t_{\text{hydrolysis}} = 48\text{h} \)  
Precipitation – decanting |
| Drying - Extrudate preparation | \( t_{\text{drying}} = 48\text{h}: \text{R.T.} \) (Room Temperature)  
The extrudates were dried at \( T = 60^\circ \text{C} \) for 1h and at \( T = 115^\circ \text{C} \) for 1.5h |
| Calcination | From 20°C to 550°C with temperature increase 1°C/min  
stay at 550°C for 5h |

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%w/w Ni</th>
<th>SSA [m²/g_{cat}]</th>
<th>( V_{\text{pMicro}} ) [cm³/g_{cat}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiZA-5</td>
<td>16.4</td>
<td>232.8</td>
<td>0.137</td>
</tr>
<tr>
<td>Ni/SiZA-15</td>
<td>16.4</td>
<td>231.6</td>
<td>0.142</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dimensions (mm)</th>
<th>Specific Volume ( V_g ) [cm³/g]</th>
<th>Apparent Density ( \rho_s ) [g/cm³]</th>
<th>Porosity ( \varepsilon_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiZA-x crushed particles</td>
<td>( 0.160&lt;d&lt;0.315 )</td>
<td>0.140</td>
<td>1.920</td>
<td>0.27</td>
</tr>
<tr>
<td>Ni/SiZA-5 large crushed particles</td>
<td>( 0.630&lt;d&lt;0.800 )</td>
<td>0.200</td>
<td>1.726</td>
<td>0.34</td>
</tr>
<tr>
<td>Large diameter Ni/SiZA-5 extrudates</td>
<td>( 1.80 \times 3.0 )</td>
<td>0.318</td>
<td>1.410</td>
<td>0.45</td>
</tr>
<tr>
<td>Small diameter Ni/SiZA-5 extrudates</td>
<td>( 1.36 \times 3.0 )</td>
<td>0.266</td>
<td>1.522</td>
<td>0.40</td>
</tr>
<tr>
<td>Small diameter Ni/SiZA-15 extrudates</td>
<td>( 1.10 \times 2.7 )</td>
<td>0.139</td>
<td>1.970</td>
<td>0.27</td>
</tr>
</tbody>
</table>

**UGent/FCh13/8-9L**

Ni/Si - PILC Catalysts

17 April 2013
The well-shaped peaks observed suggest that the montmorillonite was pillared by the organometallic compound APTEOS and thus silica pillars were introduced.

They also imply well pillared materials and nearly homogenous pillar height, while the d001-basal spacing varied between 16.22 Å to 18.03 Å for Ni/SiZA-5 and for Ni/SiZA-15, respectively.

By subtracting the thickness of a montmorillonite layer (9.6 Å) from the d001 spacing, the pillar height and the interlayer distance is defined around 7 - 9 Å.


**ACTIVITY TESTS**

✓ During benzene hydrogenation experiments, catalyst initial activities as well as their performance after prolonged time on stream were examined.

✓ All catalysts showed noticeable deactivation with time on run, as the standard experiments at 150°C clearly showed.

✓ Eq. (1) allowed the calculation of catalytic reaction rates free from deactivation effects. Arrhenius plots and activation energies were obtained for initial activity, for all the catalysts.

\[
\frac{r_T(t)}{r_T(t')} = \frac{\varepsilon(t)}{\varepsilon(t')} \quad [1]
\]

\(r_T(t)\): reaction rates at temperature \(T\) and time on run \(t\)

\(\varepsilon(t)\): activity coefficient for time on run \(t\)
The calculated activation energies are in good agreement with values of $E_{\text{act}}$ reported in the literature for other catalysts $^{8,9,10,11,12}$.

It is evident that the initial catalytic activities of the La-Ni systems for benzene hydrogenation are related to the calcination temperature and the formation of perovskite phase during their preparation.

When the catalyst was left for 62 h in hydrogen stream, its maximum activity was measured during the second experimental set (B2).

Keeping smaller time intervals, i.e., 14-17 h between experimental sets, resulted in a slower catalyst activation and the maximum activity was measured during the third set (A3).

The study of the catalyst in the later way led to more coke deposition during activation period and thus different maximum activities (B2, A3) are observed.

However, no matter how the activation took place, the performance of the catalyst for the same time on run was the same (A3-B3, A4-B4) after they had reached the maximum activity.
Initial and maximum reaction rates, \( r_0 \) and \( r_{\text{max}} \), versus calcination temperatures of the non-supported La-Ni systems at reaction \( T=110^\circ\text{C} \).

Filled symbols correspond to \( r_0 \) and open symbols to \( r_{\text{max}} \). Triangles correspond to the \( \text{LaNiO}_3\)-x-1 series, squares correspond to the \( \text{LaNiO}_3\)-x-2 series.

- Catalysts having similar XRD patterns before reduction, have similar activities, while those with only the \( \text{LaNiO}_3 \) perovskite phase present have higher activities.
- The non-supported La-Ni systems did not reach the maximum of their activities immediately after their reduction period, but after several hours on hydrogen stream because the perovskite phase was not readily reduced.
- La-Ni systems which were calcined at 600°C and formed the perovskite phase were the most active catalysts.
- The final sequence of reaction rates is consistent with the XRD patterns as far as the relative \( \text{LaNiO}_3 \) peak intensities are concerned.
Arrhenius plots obtained for initial activities of the LaNiZA and La, Ni supported on AZA catalysts

- $E_{\text{act}}$ measured are in good agreement with those reported previously for this reaction.
- LaNiZA is far more active and this suggests that La, Ni deposition on clay surface via an organic compound, although difficult, expensive and time consuming, results in a more active material.
- For La, Ni supported on AZA catalysts only Ni loading and calcination temperature affect catalyst activity and not the nature of the precursors.
- For $x\text{LaNiO}_3$/AZA-$y$ and LaNiZA catalysts, the initial activities measured after the usual reduction period were their maximum attainable activities, due to the dispersion of La-Ni on the carriers which, in turn, promoted the catalyst reduction.
**Strong Metal – Support Interaction**

 ✓ The decreased catalytic activity of the La-Ni/pillared clay calcined at 600°C can be attributed to a strong metal-support interaction between the active metals and the clay surface.

 ✓ This effect was not observed for the catalyst calcined at 500°C, as implied by the rate ratios:

\[
\frac{r^{10\text{LaNiO}_3/\text{AZA – 500}}_{\text{LaNiO}_3 - 500 - 2}}{r^{10\text{LaNiO}_3/\text{AZA – 600}}_{\text{LaNiO}_3 – 600 – 2}} = 0.55
\]

\[
\frac{r^{10\text{LaNiO}_3/\text{AZA – 600}}_{\text{LaNiO}_3 – 600 – 2}}{r^{10\text{LaNiO}_3/\text{AZA – 500}}_{\text{LaNiO}_3 – 500 – 2}} = 0.01
\]

\[r_x\text{ : reaction rates of the catalysts reported, calculated per g of Ni}\]

 ✓ These remarkable differences between the reaction rate ratios cannot be attributed to the partial destruction of the pillared clay microstructure at 600°C which resulted in 30% decrease of its specific surface area.
Increased metal loading results, generally, in increase of the average active (metal) aggregate size.

The reaction rate per metal mass should decrease with metal loading in the case of structure insensitive reaction.

However, the observed exponential increase of the reaction rate with Ni loading, suggests that this reaction is structure sensitive for the systems studied in this work.

In agreement with findings of other researchers for active metals supported on various carriers in benzene hydrogenation\textsuperscript{13,14,15}.


Evolution of the reaction rate of the \(x\)LaNiO\(_3\)/AZA-500 catalysts versus Ni loading. Dotted lines correspond to initial and maximum reaction rates of the LaNiO\(_3\)-500-2 catalyst. Reaction temperature \(T=150^\circ\text{C}\).
The calculated activation energies are between 49 and 56.4 kJ/mol and are in good agreement with values of $E_{\text{act}}$ reported in literature for other catalysts $^8,9,10,11,12$.

Catalyst activity increases with metal loading up to 12% (w/w) Ni and then decreases.

Results in line with these observations were obtained for Ni/Al$_2$O$_3$ catalysts using toluene hydrogenation as a test reaction, i.e. a maximum in activity was observed by varying the Ni content$^{16}$.

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Arrhenius plots obtained for initial activities of the xNiAZA catalysts


17 April 2013
Reaction rates determined at 125 and 150°C of the xNiAZA catalysts versus Ni loading.

- Ni is first ion exchanged and goes to the dixtrigonal holes through which it can migrate into the layer.
- Next, the nickel introduced can not migrate any more into the layers that are saturated. A gradually decreasing part of it remains within the dixtrigonal holes, loosing thus part of its activity, while the rest is sparsely distributed on the surface.
- In pillared montmorillononites prepared with calcination at high temperatures, such as AZA, the acid sites present are mainly those introduced by the pillars.
- The part of the Ni distributed on the clay surface that is situated near and on the Al-pillars is favourable for the catalytic activity of xNiAZA, as benzene is adsorbed also on the acid sites and can readily react with hydrogen adsorbed on metal sites ⁸,¹⁷.

The sharp increase of activity from 8 to 12% (w/w) Ni can thus be explained by the increase of the interlayer patches and the increasing amount of nickel that cannot migrate into the almost saturated vacant sites of the octahedral layers and is, therefore, available on the surface for reaction.

The further growth of Ni patches make some area in micropores inaccessible to benzene molecules whose kinetic diameter is 5.8Å and the catalyst activity drops.

Reaction rates determined at 125 and 150°C of the xNiAZA catalysts versus Ni loading.
Reaction rates determined at 125 and 150°C of the Alie-xNiAZA catalysts at 150°C versus Ni loading.

✓ $\text{Al}^{3+}$ (ionic radius 0.5 Å) is not large enough to block the ditrigonal holes itself, however, it has higher positive valence than $\text{Ni}^{2+}$ and it can not be ion exchanged by it. Thus, $\text{Al}^{3+}$ should migrate into the lattice upon raising the temperature above 200°C and prevent Ni from migrating into it $^{18,19}$.

✓ Catalysts ion exchanged first with $\text{Al}^{3+}$ are far more active than xNiAZA catalysts because $\text{Al}^{3+}$ ion exchange modified the clay surface and in fact created new acid sites on it, in addition to the existing ones.

✓ The initial sharp increase implies that $\text{Al}^{3+}$ ion exchange was not complete and Ni migration in the ditrigonal holes was not totally overcome with $\text{Al}^{3+}$ ion exchange (Alie-2NiAZA).

The remaining amount of the impregnated Ni is dispersed on the surface and its co-effect with the existing acid sites results in high catalytic activity of the Alie-4NiAZA.

As Ni loading further increases to 8% (w/w), Ni is randomly distributed on the surface and on the fewer available acid sites.

The higher metal activity observed for the Alie-12NiAZA can be attributed to the growth of Ni patches as Ni content increases.

The consecutive decrease in activity for the Alie-18NiAZA is a result of the pore size diminution with the increase of the size of Ni patches, as for the 18NiAZA.

Reaction rates determined at 125 and 150°C of the Alie-xNiAZA catalysts at 150°C versus Ni loading.
The carrier effect has been examined when the interlaminar space of the clay sheets is not available for reaction.

Even after Al\(^{3+}\) ion exchange, which was not complete, a number of compensating ions still remain. This explains the very low activity of Alie-4NiZ catalyst.

On raising the metal loading up to 6% (w/w) some Ni is still able to ion exchange. However, Al\(^{3+}\) has a hindrance effect for the Ni entrance in the “close structure” of the clay so that most of the Ni is situated outside the interlayer space of the meso and macropores and is available for the hydrogenation of benzene.

This results in increase in catalytic activity, in a lower extent for Alie-6NiZ where some Ni is still inaccessible as it is ion-exchanged in the interlayer space, and in higher extent for Alie-8NiZ.

Reaction rates determined at 125 and 150°C of the Alie-xNiZ catalysts versus Ni loading.
The catalysts of $x$NiATOS series showed rapid and severe deactivation during the first three hours when running at reaction temperatures close to 150°C.

Reaction rates were calculated, for benzene conversions below 6%, after the catalysts had reached a nearly constant activity.

The $x$Pas-4.2NiATOS and 4.2Ni-$x$PasATOS series of catalysts were prepared, since it is known that treatment of acid catalysts with alkaline solutions results in passivation of their strongest acid sites\textsuperscript{20}. Steady but lower than fresh 4.2NiATOS activity was observed.

The steady activity after deactivation of \( x \)NiATOS catalysts should be attributed to the loss of their strong acid sites due to coke formation.

The phosphate ligand introduced in 4.2Ni M.E.-ATOS acted as a molecular mask preventing nickel to be deposited on the edges of the clay layers. Therefore, the acid sites present on the broken edges of the saponite layers contributed neither to the catalyst activity nor to the formation of coke and rapid deactivation.

Conclusively, most of the acid sites responsible for both the extremely high activity of nickel on Al-pillared saponite as well as for its severe deactivation are those present at broken edges.

The calculated activation energies are between 42 and 53 KJ/mol and are in good agreement with values of $E_{act}$ reported in literature for other catalysts $^8, ^9, ^{17}$.

Also for these catalysts, activity depends on nickel loading.
The effect of Ni loading on the reaction rates of \( x\text{NiATOS} \) and \( x\text{NiAZA} \) catalysts determined at 150°C.

- Comparing with the \( x\text{NiAZA} \) catalysts, it is obvious that their activity dependence on nickel loading differ from that of \( x\text{NiATOS} \) catalysts.

- The origin of higher catalytic activity as well as its variation with nickel loading in the case of pillared saponite compared to pillared montmorillonite has been related to the structural differences of the parent clays \(^{21}\).

- H-K effect is not possible in pillared saponite catalysts. Catalytic performance is influenced by the way nickel is distributed on the clay surface, that is by the metal-support interactions, and not by the loss of the nickel introduced within the clay sheets.

The reasoning given for the observed two maxima in Alie-xNiAZA catalysts stands also for xNiATOS catalysts.

The first one is mainly attributed to nickel located near the substrate acid sites, while the second maximum to the growth of nickel patches in the interlayer space, up to an optimum that is still enabling the access of benzene molecules to micropores.

The main differences derive from the nature of the acid sites present in each type of material.

The Al$^{3+}$ cations inserted in Alie-xNiAZA have significantly promoted their activity suggesting that some new acid sites have been created.

The acidity of pillared saponites is mainly attributed to the clay structure$^{22}$.

---

Due to the same method of preparation and common content of Ni (16.4 %w/w), the activities observed are essentially identical when studied without the influence of mass transfer phenomena.

Common calculated activation energy of 56.4 KJ/mol, which is in good agreement with values of $E_{\text{act}}$ reported in the literature$^{8,9,10,12,17}$.
The observed diffusion coefficient of benzene versus reaction temperature,

\[ \eta = \frac{1}{\Phi}, \quad \eta \ll 1 \]

\[ \Phi = L \sqrt{\frac{(n + 1)k_{\text{int}}C_B^{n-1}\rho_s}{2D_{eB}}}, \quad n > -1 \]

\[ \frac{r_{\text{int}}}{C_B} = kC_B^{n-1}, \quad r_{\text{int}} [\mu\text{mol/g}_{\text{cat}}/\text{s}] \]

Suppose \[ C_B = C_B^S \]

\[ \frac{2}{n + 1} D_{eB_{obs.}} = \left( \frac{L}{\Phi} \right)^2 \frac{r_{\text{int}}}{C_B} \]

The form of the curve obtained (Obs.) proves the inconsistency in our original hypothesis, where the external mass transport effects were assumed insignificant.
Calculated diffusion coefficient of benzene versus extrudate porosity, at the three highest reaction temperatures.

\[
\text{De}_{\text{Calc}} \left[ \frac{2}{(n+1)} \right] \text{ [cm}^3\text{gas/cm}^3 \text{cat/s]} 
\]

Ni/SiZA-5 large diameter extrudates exhibit the highest apparent diffusivity unlike the Ni/SiZA-15 small extrudates.

Apparent diffusivity appears to linearly increase with porosity.
Comparison of hydrogenation activity

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$100^\circ\text{C}$</th>
<th>$125^\circ\text{C}$</th>
<th>$150^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3NiAl$_2$O$_3$</td>
<td>1.65</td>
<td>4.36</td>
<td>11.60</td>
</tr>
<tr>
<td>LaNiZA</td>
<td>7.01</td>
<td>16.53</td>
<td>35.21</td>
</tr>
<tr>
<td>12.6NiATOS</td>
<td>15.02</td>
<td>42.60</td>
<td>106.79</td>
</tr>
<tr>
<td>Alie-12NiAZA</td>
<td>16.79</td>
<td>54.18</td>
<td>152.19</td>
</tr>
<tr>
<td>Ni/SiZA-x</td>
<td>34.51</td>
<td>107.98</td>
<td>295.25</td>
</tr>
<tr>
<td>4.1NiVycor</td>
<td>41.73</td>
<td>122.96</td>
<td>318.86</td>
</tr>
</tbody>
</table>
Ni catalytic activity in PILCs seems to depend on the size of the metal aggregates formed on the clay surface, suggesting thus that benzene hydrogenation over these materials is a structure sensitive reaction.

Determining factor of Ni/PILC catalytic activity was the acidity of the carrier, both in terms of intensity and of its origins.

The moderate acid sites in AZA PILCs mainly due to the existence of the Al-pillars, contribute so that Ni on AZA carrier present moderate but steady activity, in cases where Ni is available for reaction and does not migrate into the montmorillonite lattice (H-K effect).

The strong acid sites of the ASTOS PILCs, which are mainly due to structural characteristics of the saponite and not to the existence of pillars, are responsible for both the extremely high activity of nickel on Al-pillared saponite as well as its severe deactivation.

For the La-Ni systems, either supported on AZA or not, the main factor influencing their activity, other than the Ni aggregate size, is their calcination temperature which determines their structure.

The Ni/PILC catalytic system with Si oxide pillars were the most active of all Ni/PILCs studied.

xNi/SiZA catalysts were almost twice as active as the best of all other catalysts, Alie-12NiAZA and equally active as the best Ni catalytic system supported on commercial Vycor glass.

The activation energies determined for all the catalysts studied are between 42 and 56.4 KJ/mol and are consistent with the values sited in the literature for other carriers tested in benzene hydrogenation reaction.
Internal and external mass transfer limitations exist during operation of Ni/SiZA-x extrudates.

The calculated apparent diffusivity of benzene increases exponentially with temperature as expected from theory, while it presented a linear increase with catalyst porosity.

The calculated activation energy of diffusion $E_D$ for the extrudates increases with the decrease of large meso and macropore volume.
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