Isobutane aromatization over complete Lewis-acid Zn/HZSM-5 zeolite catalyst: performance and mechanism


a State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

b State Key Laboratory for Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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Table S1 DFT calculation of ZnO structure inside of zeolite channel

<table>
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<tr>
<th>n</th>
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<th>3</th>
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<tbody>
<tr>
<td>ΔG (kcal/mol)</td>
<td>2.99</td>
<td>2.85</td>
<td>31.52</td>
<td>-303.28</td>
<td>-305.08</td>
</tr>
</tbody>
</table>

The thermodynamic stability of ZnO cluster inside of channel (873K)

Zeolite@\((\text{ZnO})_n\) → Zeolite + (ZnO)_n

Based on the calculation, it was found that if n is not bigger than 5, the Gibbs free energies were positive, while n is bigger than 5, the Gibbs free energies were negative. It dictates that in the intersection of ZSM5, (ZnO)₅ cluster is the biggest and stable cluster.

Figure S1 H₂-TPR profiles of ZnO reference and Zn₈.₄⁷/HZSM-5 catalyst pretreated by H₂ flow at the speed of 3ml/min for 6 hours at different temperatures.
Figure S2 Reaction stability of isobutane conversion over HZSM-5 and Zn/HZSM-5 catalysts. (a) 400°C, (b) 450°C, (c) 500°C, (d) 560°C. Reaction conditions: P=0.1 MPa, WHSV=0.75 h⁻¹.

Figure S3 Reaction stability of BTX selectivity over HZSM-5 and Zn/HZSM-5 catalysts. (a) 400°C (b) 450°C (c) 500°C (d) 560°C. Reaction conditions: P=0.1 MPa, WHSV=0.75 h⁻¹.
Figure S4 DB-FTIR profiles of isobutane aromatization on nano-sized HZSM-5, Zn$_{2.34}$/HZSM-5 and Zn$_{0.47}$/HZSM-5 catalysts at different temperatures 150-450°C and 101.33 kPa obtained using a DB-FTIR spectrometer in a flowing mixture of isobutane and nitrogen gas (2 % isobutane - 98 % nitrogen), GHSV=1080 h$^{-1}$. 
Three-dimensional DB-FTIR profiles of propene aromatization on (a) nano-sized HZSM-5, (b) Zn_{2.34}HZSM-5 and (c) Zn_{6.47}HZSM-5 catalysts at 250°C and 101.33 kPa obtained using a DB-FTIR spectrometer in a flowing mixture of propene and nitrogen gas (6% propene - 94% nitrogen), GHSV=1080 h⁻¹.
Figure S6 Geometric structures of reaction intermediates and transition states in primary activation of isobutane
(the unit for bond length is Å)
**Supplementary Information**

Path 1 and 2: propylene oligomerization over \([\text{Zn(OH)}]^+\) according to carbanion mechanism; Path 3: propylene oligomerization over \([\text{Zn}(\text{C}_3\text{H}_3)]^+\) according to carbocation mechanism

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**Zinc-Oxide-Zinc**

**Path 1 and 2:**
- \(\text{Zn}^{2+} - \text{C}_3\text{H}_2\)
- \(\text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{O} \rightarrow \text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{H} \rightarrow \text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{OH} \rightarrow \text{Zn}^{2+} - \text{C}_3\text{H}_2\)
- \(\Delta E_{\text{AH}} = -14.27\text{ Kcal/mol}\)
- \(\Delta E_{\text{TS}} = -3.91\text{ Kcal/mol}\)
- \(\Delta E = -21.04\text{ Kcal/mol}\)

**Path 2:**
- \(\text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{Zn}^{2+} \rightarrow \text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{Zn}^{2+} \rightarrow \text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{OH} \rightarrow \text{Zn}^{2+} - \text{C}_3\text{H}_2\)
- \(\Delta E = -31.08\text{ Kcal/mol}\)
- \(\Delta E_{\text{TS}} = 35.66\text{ Kcal/mol}\)
- \(\Delta E_{\text{AH}} = -30.97\text{ Kcal/mol}\)

**Path 3:**
- \(\text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{Zn}^{2+} \rightarrow \text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{Zn}^{2+} \rightarrow \text{H}_2\text{C} = \text{CH} - \text{CH}_2\rightarrow\text{OH} \rightarrow \text{Zn}^{2+} - \text{C}_3\text{H}_2\)
- \(\Delta E = -34.22\text{ Kcal/mol}\)
- \(\Delta E_{\text{TS}} = 29.88\text{ Kcal/mol}\)

**Path 4:**
- \(\text{H}_2\text{C} = \text{CH}_2\rightarrow\text{Zn}^{2+} \rightarrow \text{H}_2\text{C} = \text{CH}_2\rightarrow\text{Zn}^{2+} \rightarrow \text{H}_2\text{C} = \text{CH}_2\rightarrow\text{OH} \rightarrow \text{Zn}^{2+} - \text{C}_3\text{H}_2\)
- \(\Delta E = -34.27\text{ Kcal/mol}\)
- \(\Delta E_{\text{TS}} = 20.12\text{ Kcal/mol}\)
Scheme S2 The cyclization of propylene dimmer (formed by Path1) over (Zn-O-Zn)²⁺ active center with the participation of adjacent [ZnOH]⁺
**Scheme S3** The cyclization of propylene dimer (formed by Path 3) over (Zn-O-Zn)$^{2+}$ active center with the participation of adjacent [ZnOH]$^+$
Figure S7 Geometric structures of reaction intermediates and transition states of propylene oligomerization and cyclization (the unit for bond length is Å)