Supporting information for

Mechanism of Alkane H/D exchange over Zeolite H-ZSM-5 at Low Temperature: A Combined Computational and Experimental Study

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Table S1. The adsorption energy and intrinsic activation barriers (kcal/mol) of isobutane direct H/D exchange over 72T H-ZSM-5 zeolite model with different number of active site atoms treated as high level (See Figure S1). *

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_{ads}$</th>
<th>$E_{act}$</th>
</tr>
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<tbody>
<tr>
<td>2T (O$_3$Si-OH-AlO$_3$)</td>
<td>-10.9</td>
<td>32.5</td>
</tr>
<tr>
<td>8T ((SiO)$_3$Si-OH-Al(OSi)$_3$)</td>
<td>-11.1</td>
<td>31.8</td>
</tr>
<tr>
<td>12T ((SiO)$_2$(SiO)$_3$Si-OH-Al(OSi)$_3$(SiO)$_2$)</td>
<td>-11.2</td>
<td>31.8</td>
</tr>
</tbody>
</table>

* The structure optimizations are performed on the level of ONIOM(m062x/6-31g(d,p):mndo) with the high level atoms relaxing. Based on the optimized structures, the adsorption energy and intrinsic activation barrier are calculated on the level of m062x/6-31g(d,p).
Scheme S1. The activation energy of isobutane H/D exchange in HZSM-5 zeolite at M062X/6-31g(d,p) (in black) and ωB97dx/6-31g(d,p) (in bracket) theoretical levels.
Figure S1. Representation of H-ZSM-5 zeolite by 72T model. The 2T (a), 8T (b) and 12T (c) cluster in the extended cluster models represented as ball and stick view was treated as high-layer atoms during the ONIOM calculations.

Figure S2. Optimized geometries of transition states (TS) for isobutane direct H/D exchange over EFAL-H-ZSM-5 zeolite with the accessible EFAL species (a) AO\(^+\), (b) Al(OH)\(_2^+\) and (c) AlOH\(^2+\). Selected interatomic distances (in Å) are indicated.