A novel route to the synthesis of bulk and well dispersed alumina-supported Ni$_2$Mo$_3$N catalysts via single-step hydrogen thermal treatment

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**Supplementary Information**

**Synthesis of alumina supported Ni$_2$M$_3$N by the TPN method**

The preparation of Ni$_2$Mo$_3$N/$\gamma$-Al$_2$O$_3$ by the conventional temperature-programmed reduction method in NH$_3$ flow is described as follows:

The $\gamma$-Al$_2$O$_3$ support was impregnated simultaneously with an aqueous solution containing Ni(CH$_3$COO)$_2$·6H$_2$O and (NH$_4$)$_6$Mo$_7$O$_24$·2H$_2$O with a molar ratio of 14:3 in 15 wt % NH$_3$·H$_2$O solution with stirring for 3 h. The mixture was then filtered. The solid was dried at 393 K for 3 h, and then calcined in air at 773 K for 5 h to obtain the NiO-MoO$_3$/$\gamma$-Al$_2$O$_3$ precursor for nitrides. The supported oxides precursor was then heated in a NH$_3$ flow at a mass rate of 6500 h$^{-1}$. The temperature was increased linearly at a rate of 6 K/min from room temperature to 623 K, and then at a rate of 1 K/min to 923 K, finally kept at this temperature for 2 h. The product was naturally cooled to room temperature and passivated for 7 h in a flow of 1% (v/v) O$_2$/N$_2$ to achieve 23 wt % Ni$_2$Mo$_3$N/$\gamma$-Al$_2$O$_3$. 
### Table S1

The chemical composition of bulk Ni$_2$Mo$_3$N prepared by the hydrogen thermal method

<table>
<thead>
<tr>
<th></th>
<th>Ni content (wt %)</th>
<th>Mo content (wt %)</th>
<th>N content (wt %)</th>
<th>Elemental composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Ni$_2$Mo$_3$N</td>
<td>26.92</td>
<td>66.85</td>
<td>2.93</td>
<td>Ni$<em>{2.04}$Mo$</em>{3.04}$N$_{0.91}$</td>
</tr>
<tr>
<td>Theoretical value</td>
<td>28.00</td>
<td>68.66</td>
<td>3.34</td>
<td>Ni$_2$Mo$_3$N</td>
</tr>
</tbody>
</table>

**Fig. S1.** Bulk Ni$_2$Mo$_3$N prepared with different ramp rates by the hydrogen thermal method

**Fig. S2.** EDX pattern of Ni$_2$Mo$_3$N/Al$_2$O$_3$ prepared by the hydrogen thermal method
**Fig. S3** The synthesis processes of 23 wt % Ni$_2$Mo$_3$N supported on alumina prepared (a) by hydrogen thermal method and (b) by the conventional TPN method.