Supporting Information

Superior Reactivity of Skeletal Ni-based Catalysts for Low-Temperature Steam Reforming to Produce CO Free Hydrogen

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Experimental

**Preparation of the skeletal Ni catalysts:** Under gentle stirring, 2 g of Ni-Al alloy powder (50 wt% Ni + 50 wt% Al) was added to an aqueous solution of NaOH (120 ml, 20%) at 50 °C. The resultant mixture was stirred at 70 °C for 3 h. The precipitate was sequentially washed with distilled water and ethanol, and stored in ethanol prior to the use.

**Preparation of the skeletal Ni-based catalysts:** A certain amount of Cu(CH₃COO)₂, Co(CH₃COO)₂ and Pt(NO₃)₂ solution was added to the above skeletal Ni catalyst separately, while the volume was kept at 70ml. The solution was stirred at 70 °C for 1 h. The precipitate was washed with water till no ions were detected in the filtrate, and then it was washed with ethanol and stored in ethanol. For activity test and characterizations, all catalysts were dried at 80 °C under vacuum for 5 h and were protected under nitrogen ambient.

**Preparation of nitric acid modified skeletal Ni catalyst:** 0.5 ml nitric acid solution was added to the skeletal Ni catalyst, and the volume was kept at 70ml. The resultant solution was stirred at 70 °C for 1 h. The precipitate was then washed with water till no ions (e.g., NO₃⁻) were detected in the filtrate, and subsequently it was washed with ethanol and stored in ethanol.

**Preparation of Ni/SiO₂ catalyst:** commercial SiO₂ was calcined at 700 °C for 2 h. Ni/SiO₂ was prepared by the incipient wetness impregnation method. SiO₂ was impregnated in a Ni(NO₃)₂·6H₂O ethanol solutions by mechanical agitation at 50 °C for 12 h, followed by evaporated at 60 °C using vacuum rotary until the ethanol was removed. The resultant solid was dried at 100 °C for 12 h, and then calcined at 700 °C for 2 h. The amount of Ni loading was fixed to 15 wt%.

**Activity test:** Catalytic tests were conducted at atmospheric pressure in a quartz fixed-bed reactor loaded with 0.1 g catalyst mixed with 1 ml quartz particles. Before the test, the catalysts were reduced at 400 °C in situ for 1 h in a flow of 10 vol% H₂/N₂ (50 ml/min). The liquid solution with a water/ethanol molar ratio of 8 was fed at 0.033 ml/min (or 0.022 ml/min) through an HPLC pump into a heated chamber (150 °C) to evaporate the solution completely in the stream of N₂ (60 ml/min). The products were analysed online by two gas chromatographs. One is equipped with a FID, and a Porapak-Q column.
with N₂ as a carrier gas to analyse the organic species such as ethanol and methane. The other one is integrated with a TCD and a TDX-01 column using He as a carrier gas to monitor the incondensable gas species including hydrogen, carbon dioxide, carbon monoxide and methane.

**Characterization:** Textual properties of the catalysts were measured using a Micromeritics Tristar 3000 analyzer by nitrogen adsorption at 77K. The specific surface areas were calculated from the isotherms using the BET method, and the pore distribution and the cumulative volumes of pores were obtained by the BJH method from the desorption branches of the adsorption isotherms. Elemental analysis of catalysts was performed on an ICP-OES (Varian Vista-MPX) at a high frequency emission power of 1.5 kW and a plasma airflow of 15.0 L/min ($\lambda_{\text{Ni}} = 216.555$ nm, $\lambda_{\text{Al}} = 396.152$ nm, $\lambda_{\text{Cu}} = 324.754$ nm, $\lambda_{\text{Co}} = 238.892$ nm, $\lambda_{\text{Pt}} = 265.945$ nm). X-ray diffraction patterns were recorded with a Bruker D8 Focus operating at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation ($\lambda = 1.54056$ Å) and operating in a 2θ range of 15 - 85° at a scanning rate of 0.02 °/step and 0.15 s/step. SEM was conducted on a Hitachi S4800 field emission microscope at 10.0 kV. TEM images were obtained on a FEI Tecnai G2 F20 transmission electron microscope at 100 kV. The active surface areas were determined by H₂ pulse chemisorption (Micromeritics AUTOCHEM II 2920). After the catalyst was reduced at 400 °C for 1.0 h under 10% H₂/Ar flow, it was cooled down to room temperature under Ar, and then H₂ pulses were injected until the eluted peak area of consecutive pulses was constant. The active surface area ($S_{\text{H₂}}$) was calculated from the volume of H₂ adsorbed by assuming a H/Ni stoichiometry of 1 and a surface area of $6.5 \times 10^{-20}$ m² per Ni atom.¹ Carbon deposition analysis was carried out using a thermal analysis system (STA449F3, NETZSCH Corp.). The experiments were performed in a flow of air (50 ml/min) with a heating rate of 10 °C/min and a final temperature of 800 °C.

**Conversion, selectivity and yield calculations:**

$$X_{\text{EtOH}} = \frac{F_{\text{EtOH, in}} - F_{\text{EtOH, out}}}{F_{\text{EtOH, in}}} \times 100\%$$

$$\text{H₂ selectivity} (%) = [(\text{moles of H₂ produced})/(\text{moles of C in gas products})] \times (2/6) \times 100$$
\[ S_j = 100 \times \left( \frac{\frac{\% j \times i}{\% CO} + \frac{\% CO_2}{\% CH_4} + 2(\% C_2 H_4) + 2(\% C_2 H_6) + 2(\% CH_3 CHO) + 3(\% CH_3 COCH_3)}{(\% CO) + (\% CO_2) + (\% CH_4) + 2(\% C_2 H_4) + 2(\% C_2 H_6) + 2(\% CH_3 CHO) + 3(\% CH_3 COCH_3)} \right) \]

where \( j \) represents the carbon containing species in the products, including CO, CO₂, CH₄, C₂H₄, C₂H₆, CH₃CHO, and CH₃COCH₃. \( i \) is the number of carbon atoms in the carbon-containing species.

Ethanol conversion rate = mole flowrate of ethanol converted / mole of the active nickel in the catalyst

Product’s yield = mole flowrate of the product / mole of the active nickel in the catalyst

The carbon balance was within ±5% for all catalytic runs. Data for the catalyst activity were collected when the reaction reached stable conditions, and repeated tests have been run to confirm the activity.

It should be emphasized that according to the definitions, the sum of the selectivities of H₂ and the carbon-containing species does not lead to unity since they are calculated based on independent hydrogen and carbon balances, respectively.

References:
**Table S1.** BET properties of nitric acid modified skeletal Ni catalyst

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area / m²/g</th>
<th>Average pore diameter / Å</th>
<th>Pore volume / cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric acid modified</td>
<td>111.0</td>
<td>32.8</td>
<td>0.058</td>
</tr>
<tr>
<td>skeletal Ni</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/skeletal Ni</td>
<td>99.2</td>
<td>31.2</td>
<td>0.047</td>
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**Table S2.** Physical properties of Ni/SiO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area / m²/g</th>
<th>Average pore diameter / Å</th>
<th>Pore volume / cm³/g</th>
<th>Particle size / nm [a]</th>
<th>Crystal size / nm [b]</th>
<th>S_H / m²/g_Ni [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiO₂</td>
<td>384.3</td>
<td>32.9</td>
<td>0.24</td>
<td>7.9 ± 1.3</td>
<td>7.5</td>
<td>6.3</td>
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</tbody>
</table>

[a] determined from TEM graph (statistics on 20 particles randomly picked up from TEM graph). [b] Ni crystal size determined by the Scherrer equation from the 111 plane of Ni in XRD patterns. [c] active surface area determined by H₂ pulse chemisorption.

**Table S3.** Catalysts’ active surface area after the stability test

<table>
<thead>
<tr>
<th>Catalysts’ S_H / m²/g_Ni [a]</th>
<th>skeletal Ni</th>
<th>Cu/skeletal Ni</th>
<th>Co/skeletal Ni</th>
<th>Pt/skeletal Ni</th>
</tr>
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<tbody>
<tr>
<td>New after reduced</td>
<td>14.2</td>
<td>14.5</td>
<td>14.7</td>
<td>14.9</td>
</tr>
<tr>
<td>After 10 h reaction</td>
<td>12.0</td>
<td>13.5</td>
<td>13.7</td>
<td>13.8</td>
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<tr>
<td>After 50 h reaction</td>
<td>3.4</td>
<td>5.9</td>
<td>7.18</td>
<td>5.1</td>
</tr>
</tbody>
</table>

[a] active surface area determined by H₂ pulse chemisorption.
Figure S1. Pore distribution of skeletal Ni-based catalysts.
Figure S2. SEM images of skeletal Ni-based catalysts: (a, b) skeletal Ni; (c, d) Cu/skeletal Ni; (e, f) Co/skeletal Ni; (g, h) Pt/skeletal Ni.
Figure S3. EDAX mapping of M (Co, Pt), Ni, Al, O distribution of skeletal Ni-based catalysts in SEM images: (a) Co/skeletal Ni; (b) Pt/skeletal Ni.
Figure S4. XRD patterns of skeletal Ni-based catalysts
Figure S5. TEM images and particle size distribution of skeletal Ni-based catalysts: (a) skeletal Ni; (b) Cu/skeletal Ni; (c) Co/skeletal Ni; (d) Pt/skeletal Ni; (e) Close-up image of a nickel particle. It should be emphasized that the background is carbon foil, and the nickel particle is in
a high dispersion state. Particle size distribution is a statistical estimation based on 20 particles randomly picked up from TEM graph.

**Figure S6.** Carbon deposition on skeletal Ni-based catalysts. Reaction conditions: 1 atm, ethanol space velocity 3.1 h\(^{-1}\), ethanol in feed 4\%, S/C=4.
**Figure S7.** XRD patterns of skeletal Ni-based catalysts after 10 h reaction. Reaction conditions: 1 atm, ethanol space velocity 3.1 h\(^{-1}\), ethanol in feed 4%, S/C=4.
Figure S8. SEM images of skeletal Ni-based catalysts after 10 h reaction: (a, b) skeletal Ni; (c, d) Cu/skeletal Ni; (e, f) Co/skeletal Ni; (g, h) Pt/skeletal Ni.