Supporting Information

Efficient One-pot Valorization of Ethanol to 1-Butanol over Earth-abundant Ni-MgO Catalyst under Mild Conditions

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General Information

All chemicals were used as received from the commercial suppliers: Ethanol (GR, ≥99.8%), 1-butanol (GCS, ≥99.5%), Butyraldehyde (GCS, ≥99.5%), Ethyl acetate (GCS, ≥99.5%), 1,1-deithoxyethane (GCS, ≥99.5%), Ethyl butyrate (GCS, ≥99.5%), 1-hexanol(GCS, ≥99.5%), 2-ethyl-1-hexanol (GCS, ≥99.5%), 1-octanol (GCS, ≥99.5%), Acetone (AR, ≥99.8%), Na2CO3 (AR, ≥99.8%), Ni(NO3)2·6H2O (AR, ≥98.0%), Mg(NO3)2·6H2O (AR, ≥98.0%). All reactions were performed in a 50.0 mL Parr pressure reactor. Centrifugation of the reaction mixture was performed on Thermo LYNX6000 (3000 rpm, 5 min).

X-Ray powder diffraction (XRD) patterns of the catalysts were performed on Rigaku Ultima IVX-Ray diffractometer using Cu Ka radiation in the 2θ range from 10 ° to 90 ° at a scan rate of 2 °·min-1. Transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDX) were performed a JEM-2100F field emission electron microscope at an operating voltage of 200 kV equipped with a Gatan 832 CCD camera. Powdered samples were dispersed into ethanol solution under ultrasonic treatment for 40 min and the resulting suspension was put dropwise on a carbon film on copper grid. CO2-TPD and NH3-TPD were both conducted on Auto Chem. II2920 equipment (Micromeritics, USA). For CO2-TPD, 50 mg of sample was placed into a U-shaped quartz tube and heated from 50 °C to 800 °C at a ramping rate of 10 °C /min in a Helium atmosphere for 60 min and then cooled to 50 °C in CO2 gas for 60 min. Afterwards, heated from 50 °C to 800 °C at a ramping rate of 10 °C /min in a Helium atmosphere to desorb CO2. The data were recorded from 50 °C to 800 °C with a ramping rate of 10 °C/min, and simultaneously monitored by a thermal conductivity detector (TCD). For NH3-TPD, 100 mg of sample was placed into a U-shaped quartz tube and heated from 50 °C to 200 °C at a ramping rate of 10 °C /min in an Argon atmosphere and then cooled to 50 °C in NH3 gas for 20 min, afterwards, heated from 50 °C to 800 °C at a ramping rate of 10 °C /min in an Argon atmosphere to desorb NH3. The data were recorded from 50 °C to 800 °C with a ramping rate of 10 °C /min, and simultaneously monitored by a thermal conductivity detector (TCD). The contents of the metal Ni and Mg in the catalysts were measured using Inductively Coupled Plasma (ICP) on an Optima Emission Spectrometer (Perkin Elmer Optima 8000). The Ni species were determined by X-ray Photoelectron Spectroscopy (XPS) on a Quantum 2000 Scanning ESCA Microprobe instrument with a monochromatic excitation source of Al Ka radiation (hν = 1486.6 eV) performed under 12 kV and 4mA. H2 temperature-programmed reduction (TPR) experiments were conducted on a Micromeritics Autochem II 2920 instrument equipped with a thermal conductivity detector (TCD) and an MKS Circus 2 mass spectrometer. Samples of 50 mg were first purged with Helium at a flow rate of 60 ml/min at 80°C for 1 h and then cooled down to 50°C. H2 TPR was then conducted under Ar/H2 by raising the temperature from 50 to 800°C at a rate of 10°C /min.

Analysis of Products

The data were recorded on the TRACE DSQ GC–MS (Agilent 7890GC and Agilent 5975C inert MSD). Analysis condition: column, 40°C for 3 min, increased from 40 to 120 °C at 2 °C/min and held for 2 min, then increased from 120 to 250°C at 10°C/min, final temperature 250 °C for 1min. Column type: HP-5(30 m, 0.25 mm inner diameter). After reaction, the solids were separated by filtration and the composition of the liquid phase was analyzed by GC-MS and GC-FID. Besides the main product 1-butanol, a variety of other compounds were detected, which were comprehensively analyzed. Compounds with a similarity match higher than 90% based on GC-MS identification accounted for a total area percentage >95% in all samples (Table S7). Quantification was carried out by GC-FID with the use of calibration curves and the calibrated compounds accounted for >90 % of total products in all samples. Conversion and yield values were calculated based on the equations shown in the quantification part. During the reaction, the pressure produced an extra 5 bar at 250 °C when cooling to room temperature which indicates the formation of volatile products during reaction as well. Main compounds in the gas phase included: methane, ethylene, ethane, H2, CO, and CO2.

Recycling Test

After a typical catalytic run (0.2g Ni-MgO, 15ml ethanol, 250 °C, 5 h, 2.5 MPa helium), the catalyst was separated from the reaction solution by centrifugation and subsequent decantation. The solid was additionally washed with ethanol(3*10ml), the with acetone(1*10ml), and dried overnight at room temperature under vacuum prior to the next run.

Catalyst Preparation

The Ni-MgO catalyst precursors were prepared by a coprecipitation method. In a typical procedure, a solution containing Mg(NO3)2·6H2O and Ni(NO3)2·6H2O in deionized water (0.1 L) was slowly added to an aqueous solution (0.15 L) of Na2CO3 (0.025 mol, 1 g) at 70 °C under vigorous stirring. The pH was carefully maintained between 9 and 10 by adjusting with frequent additions of an aqueous solution of Na2CO3 (1 M). The mixture was vigorously stirred for 4 h at 70 °C. After cooling to room temperature, the suspension was filtered, and the solid was washed with deionized water. After the catalyst precursor was filtered, it was washed with deionized water until the washings were nitrate–free. The solid was dried at 80 °C overnight, and the catalyst precursor was obtained as green powder. The collected powder was calcined under air atmosphere at increasing temperatures with a heating rate of 4 °C /min to 400 °C and for 4 h at this temperature. The catalyst sample was reduced under H2 atmosphere at increasing temperatures with a heating rate of 4 °C /min to 400 °C at which it was kept for 4 h. Prior to exposure to air, the catalysts were passivated in a flow of 0.1% O2/N2 for 2 h at room temperature.
Quantification

The yield of products was calculated based on the number of carbon atoms in the product as follows: where \( n_i \) represents the number of carbons and \( C_i \) is the molar concentration of the compound \( i \), \( C_{E,\text{O}H} \) indicates concentration of ethanol before the reaction.

\[
Y_i(\%) = \frac{n_i C_i}{2C_{E,\text{O}H}} \times 100
\]

Conversion was based on the number of carbon atoms in the compounds according to the equations below, where \( C_{E,\text{O}H} \) indicates concentration of ethanol before the reaction and \( C'_{E,\text{O}H} \) indicates concentration of ethanol after the reaction.

\[
\text{Conversion(\%) = } (1 - \frac{C'_{E,\text{O}H}}{C_{E,\text{O}H}}) \times 100
\]

It should be pointed out that we identified most of the products, as substantiated by the carbon balance average (ca. 90%). The carbon balance was calculated as follows:

\[
C(\%) = \frac{2C'_{E,\text{O}H} + \sum n_i C_i}{2C_{E,\text{O}H}} \times 100
\]

STY (time space yield) values illustrated mass of 1-butanol obtained in per unit time and unit catalyst mass, and the STY values can evaluate the activity of the catalyst. The STY values were calculated as follows and the unit was \( \text{g } \text{butanol} \text{ kg } \text{cat}^{-1} \text{ h}^{-1} \):

\[
\text{STY} = \frac{m}{t \times m'}
\]

Conversion of Ethanol to 1-butanol

In a typical experiment, the catalyst (0.2 g unless otherwise stated) was placed in an intermittent high-pressure reactor (50 mL), and ethanol (15mL) were added. The reactor was sealed and placed in a heating sleeve at the desired temperature. After the indicated reaction time, the reactor was cooled down with an ice-water bath and subsequently carefully opened.
Table S1: Influence of temperature and catalyst loading on reaction performance using Ni-MgO catalyst

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Cat. loading (g)</th>
<th>Carbon balance (%)</th>
<th>Conversion (%)</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>170</td>
<td>0.2</td>
<td>89.7</td>
<td>14.7</td>
<td>3.9</td>
</tr>
<tr>
<td>190</td>
<td>0.2</td>
<td>84.6</td>
<td>22.0</td>
<td>5.4</td>
</tr>
<tr>
<td>210</td>
<td>0.2</td>
<td>82.0</td>
<td>32.9</td>
<td>7.7</td>
</tr>
<tr>
<td>230</td>
<td>0.2</td>
<td>84.0</td>
<td>40.9</td>
<td>21.0</td>
</tr>
<tr>
<td>250</td>
<td>0.2</td>
<td>84.5</td>
<td>44.3</td>
<td>23.7</td>
</tr>
<tr>
<td>270</td>
<td>0.2</td>
<td>69.8</td>
<td>61.0</td>
<td>14.4</td>
</tr>
<tr>
<td>250</td>
<td>0.3</td>
<td>71.2</td>
<td>50.4</td>
<td>15.6</td>
</tr>
<tr>
<td>250</td>
<td>0.4</td>
<td>69.1</td>
<td>53.3</td>
<td>16.9</td>
</tr>
<tr>
<td>250</td>
<td>0.5</td>
<td>63.2</td>
<td>57.9</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Table S2: Examples of different catalysts for the conversion of ethanol to 1-butanol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T(°C)</th>
<th>Device mode</th>
<th>Time (h)/GHSV (ml/(h·g&lt;sub&gt;cat&lt;/sub&gt;))</th>
<th>Conversion (%)</th>
<th>1-butanol Yield (%)</th>
<th>STY (g&lt;sub&gt;but&lt;/sub&gt;/kg&lt;sub&gt;cat&lt;/sub&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>450</td>
<td>Continuous</td>
<td>-</td>
<td>56.0</td>
<td>18.0</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Mg&lt;sub&gt;3&lt;/sub&gt;AlO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>350</td>
<td>Continuous</td>
<td>960 ml/(h·g&lt;sub&gt;cat&lt;/sub&gt;)</td>
<td>35.0</td>
<td>14.0</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Ca&lt;sub&gt;1.64-P&lt;/sub&gt;HAP</td>
<td>350</td>
<td>Continuous</td>
<td>880 ml/(h·g&lt;sub&gt;cat&lt;/sub&gt;)</td>
<td>26.0</td>
<td>18.0</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>HAP</td>
<td>330</td>
<td>Continuous</td>
<td>820 ml/(h·g&lt;sub&gt;cat&lt;/sub&gt;)</td>
<td>17.0</td>
<td>11.0</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;1.7&lt;/sub&gt;P HAP</td>
<td>300</td>
<td>Continuous</td>
<td>570 ml/(h·g&lt;sub&gt;cat&lt;/sub&gt;)</td>
<td>11.0</td>
<td>9.0</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>PdMgAlO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>200</td>
<td>Batch</td>
<td>5 h</td>
<td>3.8</td>
<td>2.9</td>
<td>369</td>
<td>6</td>
</tr>
<tr>
<td>CuMgAlO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>200</td>
<td>Batch</td>
<td>5 h</td>
<td>4.1</td>
<td>1.6</td>
<td>203</td>
<td>7</td>
</tr>
<tr>
<td>Co Powder</td>
<td>200</td>
<td>Batch</td>
<td>72 h</td>
<td>4.0</td>
<td>2.9</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Ni/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>230</td>
<td>Batch</td>
<td>22.4 h</td>
<td>41.0</td>
<td>19.5</td>
<td>187</td>
<td>9</td>
</tr>
<tr>
<td>Ni/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>250</td>
<td>Batch</td>
<td>72 h</td>
<td>27.0</td>
<td>22.0</td>
<td>79</td>
<td>10</td>
</tr>
<tr>
<td>Cu-CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>330</td>
<td>Continuous</td>
<td>-</td>
<td>67.0</td>
<td>30.0</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>Cu10Ni10-PMO</td>
<td>320</td>
<td>Batch</td>
<td>6 h</td>
<td>36.0</td>
<td>22.0</td>
<td>705</td>
<td>12</td>
</tr>
<tr>
<td>SrAp-100</td>
<td>400</td>
<td>Continuous</td>
<td>650 ml/(h·g&lt;sub&gt;cat&lt;/sub&gt;)</td>
<td>13.0</td>
<td>8.2</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>Mg-Al</td>
<td>400</td>
<td>Continuous</td>
<td>-</td>
<td>37.1</td>
<td>12.4</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>HAP</td>
<td>340</td>
<td>Continuous</td>
<td>720 ml/(h·g&lt;sub&gt;cat&lt;/sub&gt;)</td>
<td>5.0</td>
<td>3.2</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Cu/Mg/Al-HTC</td>
<td>320</td>
<td>Batch</td>
<td>6 h</td>
<td>64.0</td>
<td>29.0</td>
<td>767</td>
<td>16</td>
</tr>
<tr>
<td>Ru+NaOEt</td>
<td>150</td>
<td>Batch</td>
<td>4 h</td>
<td>46.0</td>
<td>32.0</td>
<td>1209</td>
<td>17</td>
</tr>
<tr>
<td>Cu+MgO</td>
<td>230</td>
<td>Batch</td>
<td>12 h</td>
<td>32.4</td>
<td>16.9</td>
<td>147</td>
<td>18</td>
</tr>
<tr>
<td>CaC&lt;sub&gt;2&lt;/sub&gt;</td>
<td>275</td>
<td>Batch</td>
<td>6 h</td>
<td>46.0</td>
<td>19.5</td>
<td>174</td>
<td>19</td>
</tr>
<tr>
<td>Calcium ethoxide</td>
<td>300</td>
<td>Batch</td>
<td>8 h</td>
<td>25.0</td>
<td>10.8</td>
<td>36</td>
<td>20</td>
</tr>
<tr>
<td>Cu10MMO</td>
<td>350</td>
<td>Batch</td>
<td>5 h</td>
<td>79.6</td>
<td>25.4</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>RuNi@MOF</td>
<td>170</td>
<td>Batch</td>
<td>14.5 h</td>
<td>6.2</td>
<td>4.8</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>Pd@UIO-66</td>
<td>250</td>
<td>Continuous</td>
<td>-</td>
<td>49.8</td>
<td>24.2</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>Ni-MgO</td>
<td>250</td>
<td>Batch</td>
<td>5 h</td>
<td>44.3</td>
<td>23.7</td>
<td>1880</td>
<td>This work</td>
</tr>
</tbody>
</table>
Table S3: Catalyst recycling experiments.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Conversion/%</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
<td>44.3</td>
<td>23.7</td>
</tr>
<tr>
<td>2</td>
<td>39.4</td>
<td>19.5</td>
</tr>
<tr>
<td>3</td>
<td>39.1</td>
<td>18.3</td>
</tr>
<tr>
<td>4</td>
<td>39.9</td>
<td>19.0</td>
</tr>
<tr>
<td>5</td>
<td>38.8</td>
<td>17.5</td>
</tr>
<tr>
<td>6</td>
<td>39.5</td>
<td>17.6</td>
</tr>
<tr>
<td>Regeneration</td>
<td>42.1</td>
<td>21.8</td>
</tr>
</tbody>
</table>

Reaction conditions: Ni-MgO 0.2g, ethanol 15 ml, 250 °C, 5 h, 2.5 MPa helium. A: 1-butanol B: Butyraldehyde C: Ethyl acetate D: 1,1-deithoxyethane E: Ethyl butyrate F: 1-hexanol G: 2-ethyl-1-hexanol H:1-octanol
Table S4: Leaching tests during catalyst recycling for Ni-MgO catalyst.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Ni(mg/L)</th>
<th>Mg(mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before reaction</td>
<td>14.2</td>
<td>5.9</td>
</tr>
<tr>
<td>1</td>
<td>11.6</td>
<td>4.7</td>
</tr>
<tr>
<td>6</td>
<td>11.3</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Table S5: Results of the MgO, Ni-MgO, Ni10-MgO, Ni0.1-MgO in the Guerbet reaction of ethanol to 1-butanol

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Carbon balance (%)</th>
<th>STY (gbut kg(^{-1}) cat(^{-1}) h(^{-1}))</th>
<th>Conversion/%</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>89.9</td>
<td>767</td>
<td>35.6</td>
<td>7.2</td>
</tr>
<tr>
<td>Ni-MgO</td>
<td>84.5</td>
<td>1880</td>
<td>44.3</td>
<td>23.7</td>
</tr>
<tr>
<td>Ni10-MgO</td>
<td>73.6</td>
<td>428</td>
<td>47.4</td>
<td>5.4</td>
</tr>
<tr>
<td>Ni0.1-MgO</td>
<td>88.6</td>
<td>1063</td>
<td>42.7</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Reaction conditions: catalysts 0.2 g, ethanol 15 ml, 250 °C, 5 h, 2.5 MPa helium. A: 1-butanol B: Butyraldehyde C: Ethyl acetate D: 1,1-deithoxyethane E: Ethyl butyrate F: 1-hexanol G: 2-ethyl-1-hexanol H: 1-octanol
Table S6: Acid–base properties of the MgO and different Ni-MgO catalysts determined by CO$_2$-TPD and NH$_3$-TPD

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>STY (g$<em>{\text{but}}$kg$</em>{\text{cat}}^{-1}$ h$^{-1}$)</th>
<th>Number of basic sites(µmol/g)</th>
<th>Number of acid sites(µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>767</td>
<td>346.3</td>
<td>382.9</td>
</tr>
<tr>
<td>Ni0.1-MgO</td>
<td>1063</td>
<td>390.6</td>
<td>351.0</td>
</tr>
<tr>
<td>Ni-MgO</td>
<td>1880</td>
<td>487.1</td>
<td>700.7</td>
</tr>
<tr>
<td>Ni10-MgO</td>
<td>428</td>
<td>173.3</td>
<td>432.7</td>
</tr>
<tr>
<td>Ni-MgO(uesd)</td>
<td>1547</td>
<td>415.6</td>
<td>718.5</td>
</tr>
</tbody>
</table>
Table S7: GC-MS analysis of the products.

<table>
<thead>
<tr>
<th>Retention time (min.)</th>
<th>Area Percentage %</th>
<th>Compound name</th>
<th>Similarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.453</td>
<td>0.13</td>
<td>Propane</td>
<td>90</td>
</tr>
<tr>
<td>1.519</td>
<td>0.99</td>
<td>Acetaldehyde</td>
<td>91</td>
</tr>
<tr>
<td>*1.632</td>
<td>47.10</td>
<td>Ethanol</td>
<td>93</td>
</tr>
<tr>
<td>*2.082</td>
<td>1.29</td>
<td>Butanal</td>
<td>96</td>
</tr>
<tr>
<td>*2.213</td>
<td>1.59</td>
<td>Ethyl Acetate</td>
<td>91</td>
</tr>
<tr>
<td>*2.818</td>
<td>28.16</td>
<td>1-butanol</td>
<td>91</td>
</tr>
<tr>
<td>3.010</td>
<td>0.35</td>
<td>2-pentanone</td>
<td>87</td>
</tr>
<tr>
<td>3.112</td>
<td>0.49</td>
<td>Heptane</td>
<td>87</td>
</tr>
<tr>
<td>3.399</td>
<td>0.23</td>
<td>Propanoic acid, ethyl ester</td>
<td>87</td>
</tr>
<tr>
<td>*3.758</td>
<td>0.77</td>
<td>Ethane, 1,1-dietoxy-</td>
<td>83</td>
</tr>
<tr>
<td>4.435</td>
<td>0.23</td>
<td>Butanal, 2-ethyl-</td>
<td>91</td>
</tr>
<tr>
<td>5.118</td>
<td>0.32</td>
<td>3-hexanone</td>
<td>97</td>
</tr>
<tr>
<td>5.567</td>
<td>0.17</td>
<td>Hexanone</td>
<td>97</td>
</tr>
<tr>
<td>*5.645</td>
<td>0.54</td>
<td>Butanoic acid, ethyl ester</td>
<td>94</td>
</tr>
<tr>
<td>6.148</td>
<td>0.30</td>
<td>Acetic acid, butyl ester</td>
<td>83</td>
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<td>7.196</td>
<td>0.05</td>
<td>1-butanol, 2-ethyl-</td>
<td>90</td>
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<tr>
<td>*8.603</td>
<td>7.45</td>
<td>1-hexanol</td>
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<tr>
<td>9.783</td>
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<td>Nonane</td>
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<td>1-hexanol, 2-ethyl-</td>
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<td>1-octanol</td>
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<tr>
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<td>0.41</td>
<td>Benzenesulfonamide, n-butyl-</td>
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</table>

Reaction conditions: Ni-MgO 0.2 g, ethanol 15 ml, 250 °C, 5 h, 2.5 MPa helium
*: compounds further confirmed by spiking with authentic standards. Quantification was performed based on additional GC-FID analysis using internal standard and calibration curves for compounds labeled with *
Only compounds with a similarity match higher than 80% based on GC-MS identification are listed. These accounted for a total area percentage >95%.
Fig. S1: Recycling test. Reactions: Ni-MgO (200 mg), ethanol (15 ml), 250 °C, 5 h, 2.5 MPa helium.
As was shown in the XRD pattern of fresh Ni-MgO catalyst (Fig. S2 b), the Ni(0) was not observed compared with Ni10-MgO, which can be explained by the appearance of the NiO-MgO solid solution to be reduced and small crystallite sizes of Ni(0) particles generated from the NiO phase. And the XRD pattern of fresh Ni10-MgO catalyst showed the apparent Ni(0) peak at 2 Theta=45.2, 52.7.
Fig. S3: The Ni2p\textsubscript{3/2} spectrum for fresh and used Ni-MgO catalysts.

Fig. S3 shows the Ni2p\textsubscript{3/2} spectra of fresh and used Ni-MgO catalysts, which contains the main peaks of multiplet set with nickel species at 853.7 eV, ~854.2 eV, ~855.6 eV, ~857.0eV, and their satellite peaks by 6.0eV above the main line. The main line peaks was assigned Ni(0)\textsuperscript{24}, NiO\textsuperscript{25}, Ni(OH)\textsubscript{2}\textsuperscript{26}, Ni(OH)\textsubscript{2}/MgNi\textsubscript{x}\textsuperscript{27}. Here, the nickel species was classified by two categories: Ni(0) and Ni(2+). Ni(2+) includes NiO and Ni(OH)\textsubscript{2} species. By integrating the main peak area, the ratio of Ni(0) for fresh Ni-MgO is 24.6% and that for used Ni-MgO is 24.9%. The ratio of Ni(0)/Ni(2+) for fresh and used Ni-MgO catalysts are similar.
The H$_2$ TPR profiles of calcined Ni-MgO were shown in the Fig. S4. The peak at 260 °C and 370 °C in the TPR profile of Ni/MgO could be attributed to the reduction of bulk NiO particles on the MgO surface. The broad consumption of hydrogen over 650 °C might be assigned to the reduction of Ni$^{2+}$ cations inserted into the lattice of MgO due to the formation of a solid solution during calcination. Considering the H$_2$-TPR profiles, the reduction temperature used for the preparation of the Ni-MgO catalysts was chosen as 400 °C, in order to reduce NiO particles, although this temperature is not enough for reducing Ni$^{2+}$ in the solid solution, and minimize metal sintering$^{28-31}$. 

![H$_2$-TPR curves of the calcined Ni-MgO catalyst.](image)
Fig. S5: CO$_2$-TPD (a) and NH$_3$-TPD (b) profiles of the investigated catalysts.
Fig. S6: The relation of STY values and numbers of basic sites in MgO, Ni0.1-MgO, Ni-MgO and Ni10-MgO catalysts.
Fig. S7: TEM images of the fresh Ni-MgO (a, b), Ni0.1-MgO (c, d) and Ni10-MgO(e,f) catalysts, EDS(g) and Ni element mapping (h) of the fresh Ni-MgO.
Fig. S8: The Ni2p3/2 spectrum of Ni10-MgO, Ni-MgO and Ni0.1-MgO catalysts.

Using the same analysis method in Fig. S3, the ratio of Ni(0) for Ni10-MgO is 28.4% and that for used Ni-MgO is 24.9%. In Ni0.1-MgO catalyst, due to the low loading of Ni on the MgO support, the ratio of Ni(0) drops to 14.7%. Except for the Ni(0) species, the others are Ni(2+) species, including NiO and Ni(OH)2.
Reference: