Electronic Supplementary Material (ESI) for Green Chemistry.

A Stable and Practical Nickel Catalyst for the Hydrogenolysis of C-O Bonds

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General: Unless otherwise stated, all compounds in table 1, table 2 and table 3 were obtained commercially from various chemical companies such as Sigma Aldrich, TCI and Fluorochem and used without any purification. The chemicals in Scheme 1 were ordered from different companies [2a (TCI, B0433), 3a (fluorochem, 210350), 4a (sigma Aldrich, OTV000198), 5a (sigma Aldrich, OTV000246)]. For the GC Conversion and yields were determined by GC-FID, HP6890 with FID detector, column HP530 m x 250 mm x 0.25 μ m. NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers.

Characterization: High-resolution TEM analysis was carried out on a JEM 2010 operating at 200 KeV. The catalyst samples after pretreatment were dispersed in methanol, and the solution was mixed ultrasonically at room temperature. A part of solution was dropped on the grid for the measurement of TEM images. XRD measurements are conducted by a STADI P automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting Cu Kα1 radiation and a 6° position sensitive detector (PSD). The XRD patterns are scanned in the 2θ range of 10-80°. For the data interpretation the software WinXpow (STOE) and the database of Powder Diffraction File (PDF) of the International Centre of Diffraction Data (ICDD) were used. The XPS measurements were performed with a VG ESCALAB 210 instrument provided with a dual Mg/Mg anode X-ray source, a hemispherical capacitor analyser and a 5 keVAr^+ ion-gun. All spectra were recorded using non-monochromatic Mg Ka (1253.6 eV) radiation. Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Ag and Mo contents of the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage ThermoJarrel Ash device.

Catalyst Recycling Experiments:

In a 4 mL glass vial, the magnetic stirring bar, the catalyst (20 mg), Lewis acid (5 mol%), biphenyl ether (0.5 mmol) and solvent (isopropanol) were added. The reaction vials were fitted with cap and needle and then were placed into a 300 mL autoclave. The autoclave was flushed with H_2 three times at 10 bar pressure and then it was pressurized to 20 bar H_2. The autoclave was placed into an aluminum plate, heated to desired temperature and the reactions were stirred for 6 h. When the reaction was finished, the autoclave was cooled to room temperature. Next, standard was added to the mixture as external standard and the mixture was diluted with ethyl acetate (20mL) followed by filtration and then analyzed by GC and GC-MS. The catalyst was separated by rotary evaporation of the solvent and products and used without further reactivation or purification for the next run.

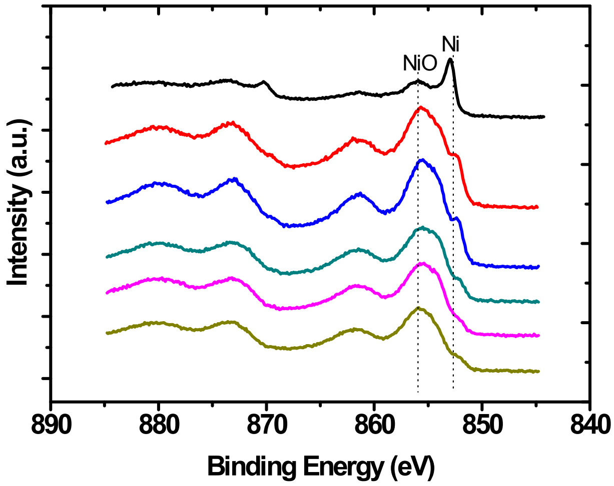


Figure S1. XPS spectra of NiAlO$_x$ catalysts, the catalysts were Ni$_{1.0}$Al$_0$O$_0$, Ni$_{0.92}$Al$_{0.08}$O$_x$, Ni$_{0.89}$Al$_{0.11}$O$_x$, Ni$_{0.87}$Al$_{0.13}$O$_x$, Ni$_{0.80}$Al$_{0.20}$O$_x$ and Ni$_{0.67}$Al$_{0.33}$O$_x$ from the topside.

Further characterization of the catalyst samples by XPS confirmed the observation from XRD diffraction patterns, i.e. more NiO formed with the addition of more AlO$_x$, Fig. S1. However, we can not get more information due to the oxidation occurred on catalyst surface during transportation in air.

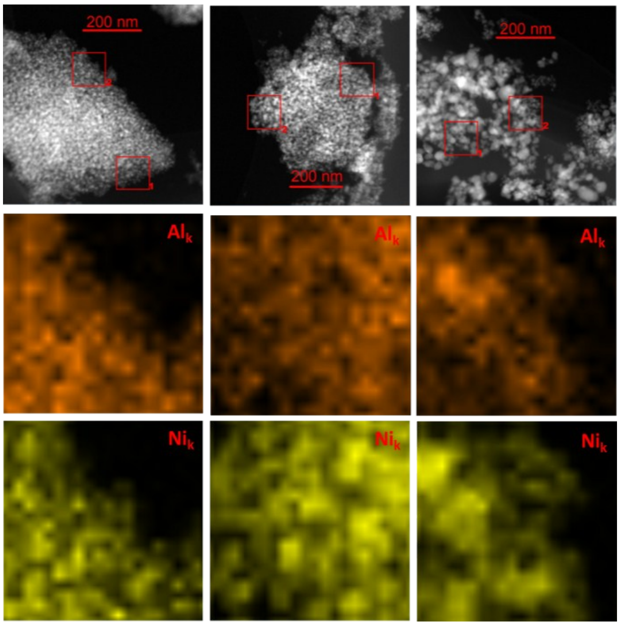


Figure S2. STEM-EDS elemental maps of catalyst samples Ni$_{0.92}$Al$_{0.08}$O$_x$, Ni$_{0.86}$Al$_{0.14}$O$_x$ and Ni$_{0.67}$Al$_{0.33}$O$_x$.

Table S1. Phenol hydrogenation catalyzed by $NiAlO_x$ with different Ni-Al ratio [a]

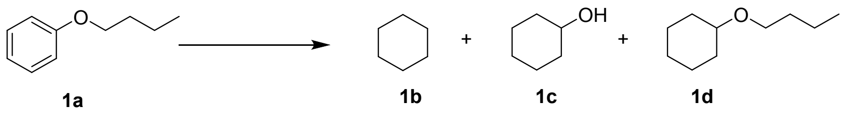
Entry	Catal./mg	Ni:Al [b]	Conv./% [c]	Sel./% [c]	Yield/% [c]
1	$Ni_{1.0}Al_0O_0$	1 : 0	16	88	14
2	$Ni_{0.92}Al_{0.08}O_x$	10 : 1	43	84	36
3	$Ni_{0.89}Al_{0.11}O_x$	8 : 1	53	92	49
4	$Ni_{0.87}Al_{0.13}O_x$	6 : 1	72	96	69
5	$Ni_{0.80}Al_{0.20}O_x$	4 : 1	55	93	51
6	$Ni_{0.67}Al_{0.33}O_x$	2 : 1	18	78	14
7	$Ni_{0.0.50}Al_{0.50}O_x$	1 : 1	32	91	29
8 [d]	$Ni_{0.87}Al_{0.13}O_x$	6 : 1	>99	>99	>99

[a] 1 mmol phenol, 44-63 mg catalysts (~0.05 mmol Ni, 5% mol Ni to phenol), 2 mL hexane, 1 atm H_2, 60 °C, 24 h. [b] molar ratio. [c] Determined by GC-FID using biphenyl as external standard material. [d] The reaction was performed at 70 °C.

The $NiAlO_x$ catalyst was tested for the industrial important benchmark of hydrogenation of phenol, which is of interest for bulk polyester processes and showed some activity on the formation of cyclohexanol. A series of Ni based catalysts was prepared with Ni-Al molar ratios from 2 : 1 to 10 : 1.

These catalysts were tested in phenol hydrogenation at ambient hydrogen pressure and the results were given in Table S1. Among all the catalysts screened, low activity was observed with $Ni_{1.0}Al_0O_0$ as catalyst. The yield of cyclohexanol was 14% (Entry 1). Subsequently, AlO_x was added to test if the catalytic activity of NiO_x can be promoted. In order to get comparable results with similar Ni loadings to phenol, 44 mg to 63 mg catalysts with different Ni-Al ratios were employed in the following measurements. Clearly, the catalytic performance can be improved significantly with the addition of AlO_x and the peak activity was obtained when the molar ratio of Ni to Al is about 6 : 1 (Entries 2-4). Less active catalysts were obtained if further increasing the AlO_x contents. Only 14% yield of cyclohexanol was detected if the ratio of Ni to Al reached 2 : 1 (Entries 5-7). Noteworthy, the phenol can be quantitatively converted into cyclohexanol just by performing the reaction at 70 °C (Entry 8). Therefore, the catalytic hydrogenation of phenol was realized at ambient hydrogen pressure in the presence of a simple $NiAlO_x$ non-noble metal catalyst!

Table S2. The effect of the Lewis acids [a]



Entry	LA	mol%	Con.(%)	Sel. (%)		
				1b	**1c**	**1d**
1	$La(OTf)_3$	1%	100	4	56	40
2	$La(OTf)_3$	3%	94	5	69	26
3	$La(OTf)_3$	5%	95	3	79	18
4	$La(OTf)_3$	10%	60	3	73	24
5 [b]	$La(OTf)_3$	5%	0	0	0	0

[a] Reaction conditions: 0.5 mmol butyl phenyl ether. 20 mg catalyst, 2mL IPA, H_2 (40 bar), $La(OTf)_3$ (1-10 mol%), 130 °C, time 6 h, conversion and selectivity were determined by GC-FID. [b] without any catalyst.

The catalytic activity for the hydrogenolysis of butyl phenyl ether was influenced by the amount of the LA added. As shown in Table S2, full conversion and lower selectivity to the desired cyclohexanol was obtained in the presence of 1 mol% $La(OTf)_3$. However, if the reaction was applied in the presence of more LA, the conversion decreased with the selectivity increasing. These results indicated that the hydrogenation of aromatic rings was inhibited in the presence of Lewis acids.

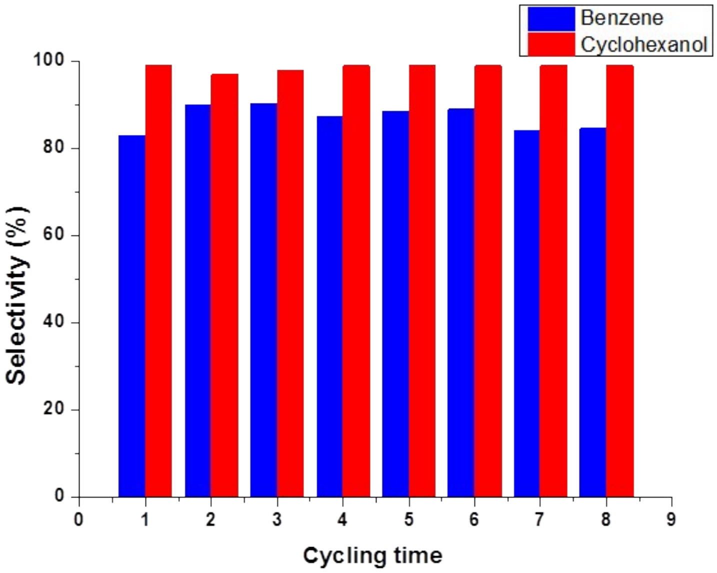


Figure S3. Hydrogenolysis of biphenyl ether: recycling of the $Ni_{0.87}Al_{0.13}O_x$ catalyst. Reaction conditions: 0.5 mmol biphenyl ether. 20 mg catalyst, 2mL IPA, H_2 (20 bar), $La(OTf)_3$ (5 mol%), 130 ^oC, time 6h.

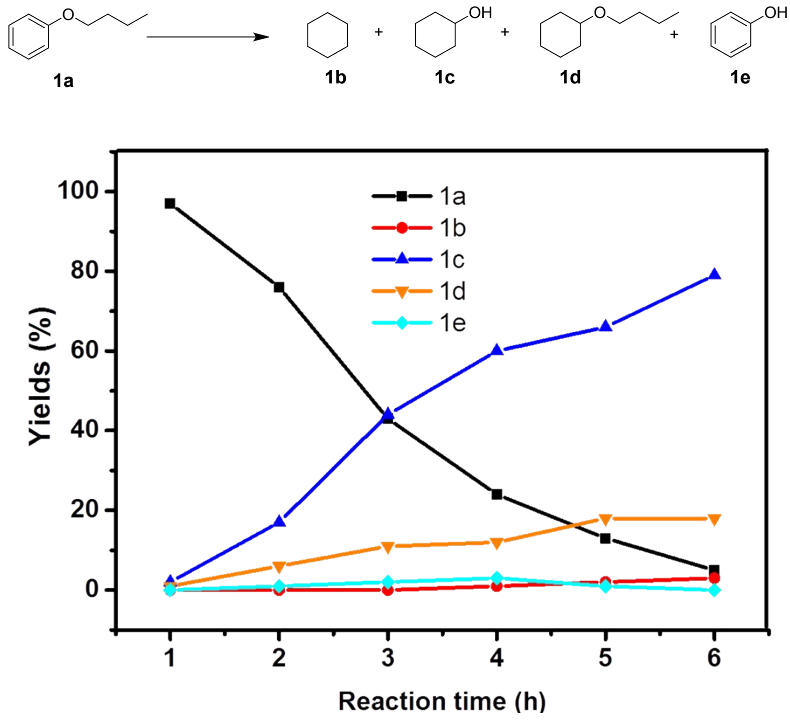
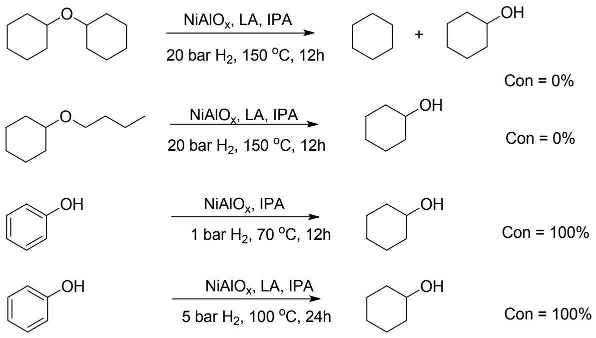


Figure S4. Conversion of butyl phenyl ether (**1a**) and yields of **1b**-**1e** as a function of reaction time.

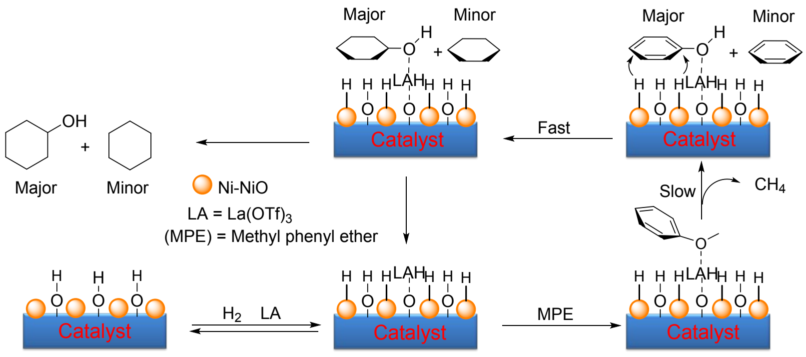
As shown in Figure S4, the conversion of **1a** proceeded smoothly and was almost finished after 6h leading to **1c** and **1d** in 79% and 18%, respectively. Meanwhile, catalytic C-O cleavage with the formation of cyclohexane (**1b**) was observed in only 3% yield. Moreover, the formation of the phenol (**1e**) was detected which might be the intermediate. From these results, we assume that the Ni catalyst combined with Lewis acid catalyzes the C-O cleavage of aromatic ethers preferentially giving phenol, which is subsequently hydrogenated to cycohexanol.

Mechanistic investigations:



Scheme S1. Control experiments on the reductive C-O cleavage.

To provide more details on the reaction mechanism, several control experiments were performed under the optimized conditions in the presence of $La(OTf)_3$. As shown in Scheme S1, no hydrogenolysis of bicyclohexane ether occurred. The same result was obtained using butoxycyclohexane as the starting material. These results indicate that the product is not generated from these aliphatic ethers and the reductive C-O cleavage occurred prior to the arene hydrogenation. Furthermore, the hydrogenation of phenol can be performed under 1 bar H_2 in the absence of LA (Scheme 1 and Table S1).



Scheme S2. Proposed reaction mechanism of the hydrogenolysis process.

Figure S5. The exemplary crude chromatogram of the reaction for entry 1, table 1.

The peak of 1 b was overlapped with solvent peak.

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                                                    Inj Volume : 1 µl
    Method          : C:\CHEM32\1\DATA\2015-05-06 16-31-46\XJC.M (Sequence Method)
    Last changed    : 5/6/2015 4:31:48 PM by SYSTEM
    Method Info     : 80/2/10-160/0/15-240/0/15-300/5; Split 70/1; inj:260; det:310; 1,5ml/min
                      const.flow

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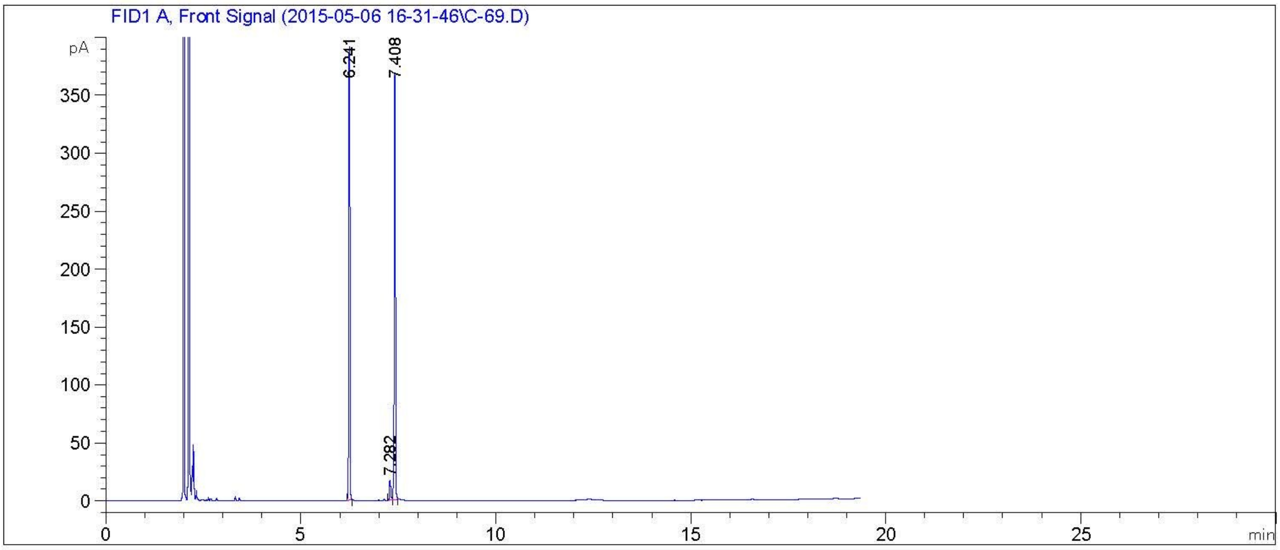

Figure S6. The exemplary crude chromatogram of the reaction for entry 2, table 1.

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                                                     Inj Volume : 1 µl
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    Last changed     : 5/18/2015 6:24:32 PM by SYSTEM
    Method Info      : 80/2/10-160/0/15-240/0/15-300/5; Split 70/1; inj:260; det:310; 1,5ml/min
                       const.flow

    Additional Info : Peak(s) manually integrated
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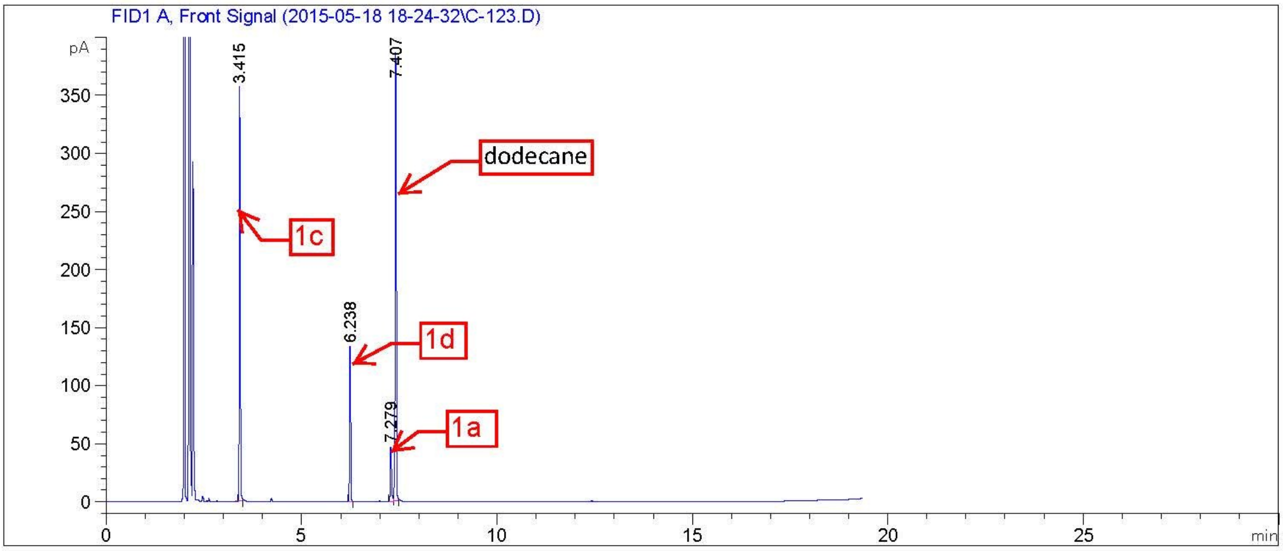

Figure S7. The exemplary crude chromatogram of the reaction for entry 4, table 1.

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                                                     Inj Volume : 1 µl
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                      const.flow

    Additional Info : Peak(s) manually integrated
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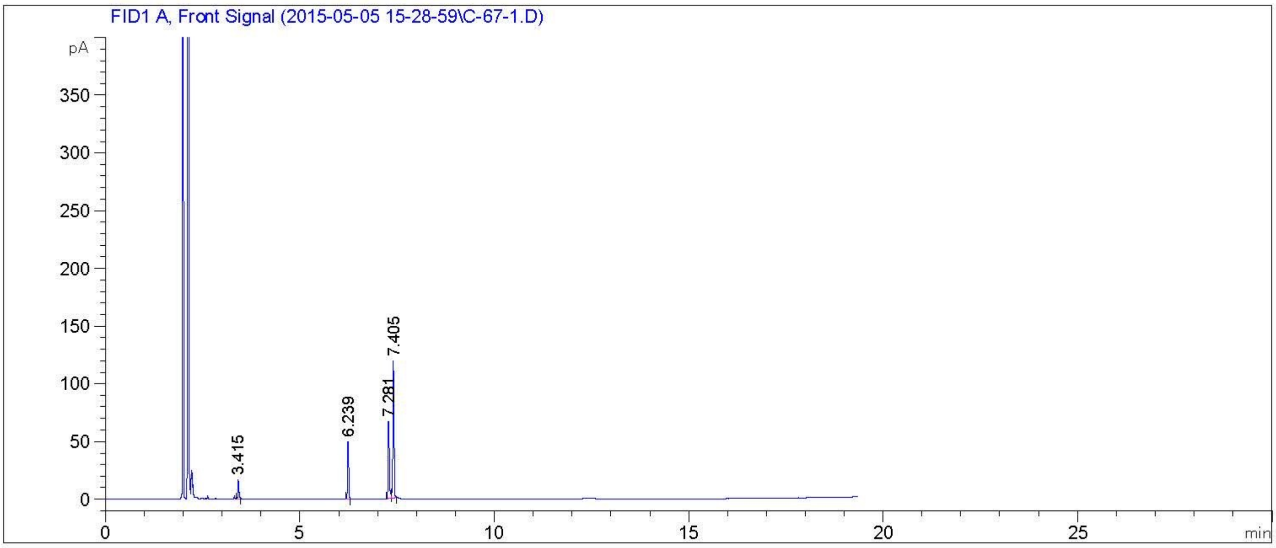

Figure S8. Measurement of methane gas.

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Data File C:\CHEM32\1\DATA\2015\1510\151026\SIG1001705.D
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                                                    Inj Volume : Manually
    Acq. Method     : C:\CHEM32\1\METHODS\SAUERSTOFFMESSUNG.M
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    Last changed    : 10/26/2015 3:05:14 PM by AK
                      (modified after loading)
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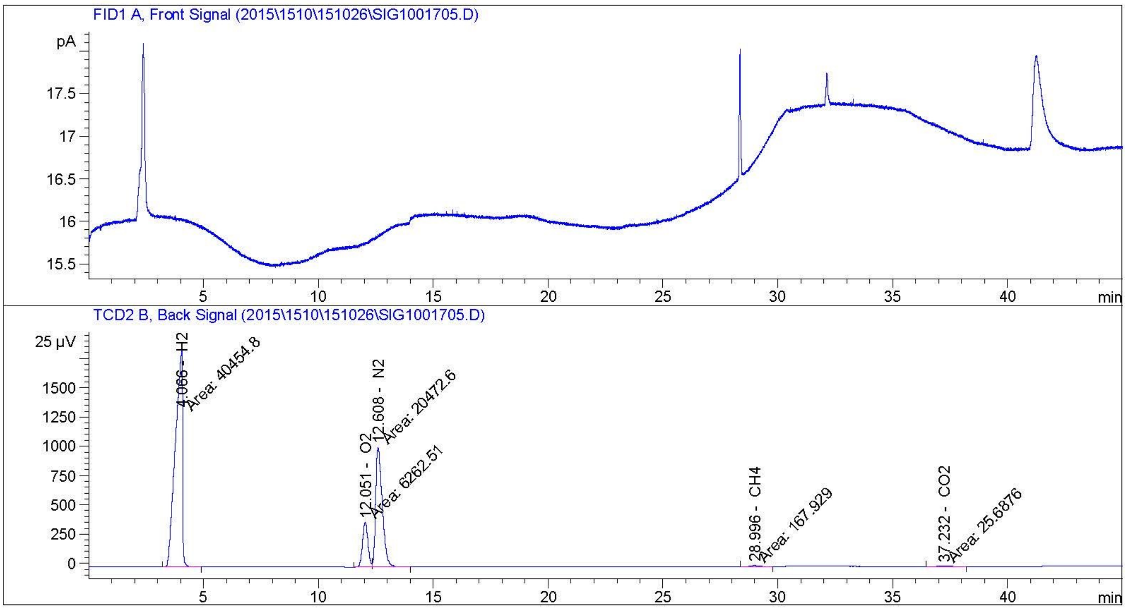

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                          External Standard Report
    =====================================================================

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    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal


    Signal 2: TCD2 B, Back Signal

    RetTime  Type     Area      Amt/Area     Amount   Grp   Name
     [min]          [25 µV*s]              [% Vol.]
    -------|------|----------|----------|----------|--|------------------
      4.066 MM     4.04548e4  3.09182e-4   12.50790     H2
     12.051 MF     6262.50586 2.89078e-3   18.10354     O2
     12.608 FM     2.04726e4  3.30591e-3   67.68056     N2
     18.000            -          -           -         CO
```

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Data File C:\CHEM32\1\DATA\2015\1510\151026\SIG1001705.D
Sample Name: cui-700

    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [25 µV*s]              [% Vol.]
    -------|------|----------|----------|----------|--|------------------
     28.996 MM      167.92918 1.07861e-3 1.81130e-1    CH4
     37.232 MM       25.68760    0.00000    0.00000    CO2

    Totals :                               98.47313


    2 Warnings or Errors :

    Warning : Calibrated compound(s) not found
    Warning : Negative results set to zero (cal. curve intercept), (CO2)

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                              *** End of Report ***
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[1] a) R. R. Deshmukh, J. W. Lee, U. S. Shin, J. Y. Lee, C. E. Song, *Angew. Chem. Int. Ed.* **2008**, *47*, 8615-8617; b) H. Z. Liu, T. Jiang, B. X. Han, S. G. Liang, Y. X. Zhou, *Science* **2009**, *326*, 1250-1252.